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RESEARCH PAPER RP1102

Part of Journal of Research of the National Bureau of Standards, Volume 20, June 1938

AN ELECTRIC HYGROMETER AND ITS APPLICATION TO RADIO METEOROGRAPHY

By Francis W. Dunmore

ABSTRACT

In radio meteorography the accuracy in measuring humidity has been considerably less than in measuring temperature. This is due to the serious time lag in the response of the hair hygrometer to sudden humidity changes encountered by a rapidly-ascending balloon. This lag increases with a decrease in temperature, so that the accuracy of this type of hygrometer becomes progressively less with increasing altitude.

This paper, which is in the nature of a progress report, deals with the development of an electrical-type hygrometer without moving parts or appreciable lag. Such an instrument makes possible a more rapid rate of ascent, and humidity measurements can be made at higher altitudes. The unit is in the form of a resistor which is connected to the input of the audio oscillator used in the radio meteorograph. The variations in the resistance of this unit with humidity are translated into audio frequencies which are received and recorded on the ground on a graphic audio-frequency recorder. The humidity-controlled resistor consists of the roughened glass surface between a dual winding on a thin-walled glass tube. The characteristics of such a unit with the roughened glass surface coated with various salts and acids are given. It was found that units so coated have a long- and short-period aging characteristic.

The effect of temperature on 11 units with different coatings is shown. The results indicate that a family of humidity-resistance curves for different temperatures may be established for a unit of standardized design. Knowing the temperature, the proper curve may be used when determining humidity from the received audio frequency.

Circuit arrangements are given showing the possibility of connecting one or more units into the oscillator circuit.

A method of expanding the humidity scale, not possible with the hair hygrometer, is shown, whereby if two or more units are used with different percentages of salt or acid coatings, each unit may be made to cover the full frequency (humidity) scale of the graphic frequency recorder for different temperature ranges.

A satisfactory unit appears to be one consisting of a dual winding of size 38 AWG tinned copper wire, 20 turns per inch, on a 0.3-mm wall Kimble flint-glass tube, 10 mm in diameter and 12.7 cm long. A coating of from 0 to 10 percent of a saturated solution of lithium chloride and water [1] may be used, depending on the aging time and the number of units necessary to cover the full temperature range. If used a day or so after coating, a unit coated with 0.5 percent LiCl would be satisfactory, or if two units are used, one should be coated with 0.25 percent and the other with 1.0 percent LiCl. A flight test using two units coated with 0.5 and 2.0 percent LiCl, respectively, in comparison with the hair-type hygrometer, indicated marked changes in humidity which the hair unit could indicate only slightly about 2 minutes later. As an ascent rate of 1,100 ft per minute was used, the hair unit was actually some 2,200 ft above the point where the real change in humidity occurred.

[1] Hereafter where percentage of coating is given, it refers to the percentage by volume of a saturated solution and water.

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I. INTRODUCTION

In the measurement of humidity in the upper atmosphere with the radio meteorograph developed by Diamond, Hinman, and Dunmore,[1] temperature inversions have indicated the probability of sudden changes in moisture content of the atmosphere encountered by the rapidly-ascending balloon, which the hair-type hygrometer failed to record. Such lag, which is a generally acknowledged defect of the hair-type hygrometer, manifests itself in incorrect humidity indications at any given altitude, depending upon the rate of ascent of the balloon, the sharpness of the humidity front, and the air temperature. The capillary-tube electrolytic type of temperature indicator responds to small temperature changes much quicker than the hair hygrometer will respond to humidity changes. It has been necessary, therefore, to limit the rate of ascent of a balloon carrying a hair-type hygrometer in order to give the hygrometer sufficient time to respond. Furthermore, the hair hygrometer ceases to function below temperatures of −20° C (approximately 25,000-ft. altitude). The hair hygrometer also requires mechanical linkages and moving parts in order to translate humidity changes into resistance variations necessary to alter the radio-meteorograph signal. Because of these limitations in the hair-type hygrometer, an investigation was started to develop a humidity indicating device which should function electrically, without moving parts or appreciable lag, and operate at stratosphere temperatures. A high rate of ascent is preferable in most instances as the data are obtained more quickly and the balloon does not drift as far away. This results in a stronger signal and greater chance of recovery.

No unit was found which would maintain a satisfactory calibration when exposed to varying humidities for long periods. Weaver and Ledig had the same experience in their work on electrical-type hygrometers.[2] The present paper, which is in the nature of a progress report, describes the development of a type of unit which, if held at a fixed humidity and subsequently checked within a few days before being used, should serve to indicate a relative humidity with an approximate

[1] H. Diamond, W. S. Hinman, Jr., and F. W. Dunmore, *A method for the investigation of upper-air phenomena and its application to radio meteorography.* J. Research NBS **20**, 369 (1938) RP1082.

[2] E. R. Weaver and P. G. Ledig. *Detector for water vapor in closed pipes.* Tech. Pap. BS **17**, 637 (1923) T242.

accuracy of ±5 percent. The speed of response of this unit is equivalent to that of the capillary-tube electrolytic thermometer, and its electrical resistance varies inherently with humidity. The effect of aging and low temperatures, and a comparison of its speed of response with that of the hair hygrometer, are described. The application of the dual-coil unit to the radio meteorograph previously mentioned is discussed. Flight records, both independently and with the hair hygrometer, are shown.

II. GENERAL DESIGN DETAILS

After experimenting with many types of electrical hygrometer resistor designs, a unit was made consisting of two fine copper wires spirally wound simultaneously on an etched glass tube. The wires were spaced about . :nm apart and the glass surface between them was found to have a resistance which varied greatly with the moisture content in the air. Tests with this unit showed it to be superior to any types previously tried, so an extensive series of experiments were made to study and improve the operation of this dual-coil glass hygrometer device. Studies were made of different kinds of glass and various types of glass surfaces, such as sandblasted, ground, and etched. The effect of varying the size and wall thickness of the glass tubing was also studied. Various types of wire were tried, such as copper and tinned and amalgamated copper. Thin adsorbent surface coatings, such as bentonite, zeolite, silica gel, clays, doucile, aluminum oxide, and gelatin were tried on the glass. Cellulose acetate; polyvinyl alcohol and acetate; hydrogel; and sodium silicate were also tried. These materials were used with different binders, such as spar varnish, shellac, paraffin, collodion, balata, instrument lacquer, and resins. The adsorbent coatings were also applied over these materials as a base. Of the salts, only the more hygroscopic were tried, such as calcium, zinc, and lithium chloride. Sulfuric and phosphoric acid were tried. Some of the above materials were used in combination with one another to lower the crystallizing point, such, for example, as a 4-percent solution of zinc chloride and a 0.35-percent solution of sulfuric acid.

III. METHODS OF MEASURING THE RESISTANCE OF THE HYGROMETERS

A study of all units under different conditions of humidity and temperature was made by measuring their resistance. Some of the measurements extended over a period of several months in order to study the effect of aging.

In making resistance measurements of a device of this type, a counter-electromotive force is developed which gives an apparent resistance of the unit greater than its true value. In studying the performance of the units, an a-c bridge or a d-c bridge or ohmmeter provided with a mechanical reversing switch, may be used to measure the true ohmic resistance. Even with this arrangement the resistance is still a function of the current flowing through the sample while making the resistance measurement. For the purpose for which this unit is designed, however, small differences between a-c and d-c resistance values are not important.

A method of measurement can be employed in which the current through the sample is pulsating direct current and is kept very small, i. e., less than a few microamperes, and the voltage impressed on the sample during measurement is large relative to the counter-electromotive force. This method consists in putting the unit in the control grid of a relaxation oscillator circuit, and from the frequency of oscillation the resistance can be determined by the substitution method. In this method the hygrometer unit is used in a circuit similar to that in which it is used in practice.

Another method (and the one used in measurements described in this paper) made use of a direct-reading ohmmeter with a scale reading from 500 ohms to 25 megohms. A motor-driven reversing switch was used in series with the circuit from the ohmmeter to the hygrometer resistor unit. While resistance readings taken on two different scales of the ohmmeter were not entirely in agreement when measuring some units, because of different currents through the unit, the two could be averaged for the purpose of the study being made.

For measuring the resistance of units of the nature here described, a proper instrument would be direct-reading, in which alternating current is applied to the sample with means for holding the same current through the sample under all conditions of measurement. The value of current adopted should be of the same order as that used in actual service.

IV. TYPES OF DUAL-COIL HYGROMETER UNITS

1. ADSORBENT COATINGS ON NONADSORBENT SURFACES

Although glass had been found to be a very effective medium for water-vapor adsorption, some preliminary experiments were made in which the glass was used merely as a coil form and did not enter into the functioning of the unit.

In these experiments, several glass tubes (smooth surface) were coated with different water-resistant substances in order to find the best coating for covering the glass to insulate it from water vapor. The tubes were then wound with the standard dual-coil winding and placed in a damp chamber and resistance readings taken at intervals. Table 1 shows the results of these measurements. The figures shown are inversely proportional to the resistance of the units. It will be noted that after 23 hours in damp air the balata (rubber) unit maintained the highest resistance. Paraffin and spar varnish came next, followed by collodion, shellac, Bakelite resin, instrument lacquer, Cellophane, glyptal rosin, and soda-lime glass, in the order given. This table shows what a good conductor (relatively) glass is, when exposed to moisture. It will be seen that balata formed the best coating. This substance was therefore dissolved in benzene and painted on the glass surface in order to keep the glass dry. Then an overcoat of adsorbent materials, such as bentonite, etc., was applied. The unit was then sanded and wound. None of the units so constructed took on enough water vapor to lower the resistance to a measurable value at the lower humidities, so work along this line was discontinued and future experiments made with the glass as the conducting surface.

TABLE 1.—*Relative variation in conductivity of various substances when exposed to moisture. Absorption characteristics (arbitrary units)*

Elapsed time	Coating on glass									
	Balata	Shellac	Paraffin	Glyptal rosin	Cellophane	Unetched soda-lime glass	Spar varnish	Collodion	Bakelite rosin	Instrument lacquer
Hours										
0	0.45	0.47	0.47	0.65	0.45	0.60	0.47	0.50	0.47	0.50
0.5	.47	.50	.47	.67	.80	80.00	.52	.62	1.30	1.00
1.0	.60	.60	.55	.85	2.00	210.00	.65	.83	3.50	1.90
2.0	.72	.80	.75	1.80	2.60	400.00	.95	1.20	5.00	5.00
4.0	1.00	1.30	1.20	4.50	4.80		1.30	1.90	2.70	4.40
23.0	4.7	9.50	5.00	70.00	22.00	3,400.00	5.00	5.50	14.00	16.00

2. GLASSES AND COATINGS

Since a roughened glass surface was found to take on water vapor very readily, dual coils were wound on glass tubing with surfaces roughened by grinding, by sandblasting, and by etching with hydrofluoric acid. No appreciable difference could be noted in the behavior of units so treated, except that roughening is quite necessary. Such roughening lowers the resistance of the sample by exposing a greater area of glass to the water vapor and by exposing a part of the glass that has not previously aged because of exposure to air. It also tends to hold any coating which may be applied to the surface.

Different types of glass were found to behave quite differently, so a study was made of dual coils wound on Kimble standard flint glass, Pyrex, Corning 0.015 glass, and soda-lime glass. The Kimble standard flint glass was found to give the most consistent results under changing temperature conditions. Since the glass tubing must be at the temperature of the surrounding air to give a true relative-humidity indication, it is necessary to use a very thin-walled tubing. Such a tubing was found as a special product of a leading glass manufacturer. It has an outside diameter of about 10 mm, a wall thickness of 0.3 mm, and a length of 12.7 cm. The outer surface of each tube was roughened by sandblasting.

These tubes were wound with size 38 AWG tinned copper wire by setting a lathe to cut a 20-turns-per-inch thread and guiding the two wires (from separate spools) through two slots in a brass fixture held in the tool post. The two slots should be approximately $\frac{1}{10}$ inch apart. The two wires are held in position at the start and finish by tying them to the tube with thread. After the unit is wound, the two wires at each end are pulled around the tube slightly in order to separate them. The thread and ends of winding are coated with a good insulating binder, such as balata or collodion. The two wires at one end of the tube are cut off close to the tube. The ends at the other end of the glass tube are soldered to terminal leads anchored to a small wooden stick supporting the glass tube. This type of construction allows free passage of the air both inside and outside of the glass tube, so that it may quickly come to the air temperature. Figure 1 (at the left) shows a unit constructed as described above. The tinned wire was adopted after experimenting with units wound with copper and amalgamated copper wire. Platinum wire would

be preferable, but it is too costly. Tin is less subject to corrosion than copper or mercury, and will therefore keep a better electrical contact with the glass.

It was first thought that the ability of the glass to adsorb water vapor might be accentuated by covering its roughened surface with some highly-adsorbent materials, such as silica gel, aluminum oxide, doucile, bentonite, clay zeolite, gelatins, etc. These were each painted on different glass units before winding, after being finely powdered and mixed with various binders, such as spar varnish, shellac, collodion, balata dissolved in benzene, and rosins. After drying the coating, the surface was rubbed with fine sandpaper in order to take off the top surface of the binder.

After testing all of these combinations, it was found that they offered no improvement over the glass used alone, and, moreover, reduced the rapidity of response to humidity changes. The same was also true for coatings of cellulose acetate, polyvinyl alcohol, polyvinyl acetate, hydrogel, and others. Sodium silicate (water glass) had a very marked effect in producing a more sensitive unit but was found very unstable and had serious temperature effects.

V. CHARACTERISTICS OF GLASS UNITS COATED WITH HYGROSCOPIC SALTS AND ACIDS

In order to study the behavior of glass units coated with various salt and acid-water mixtures in different concentrations, different units were made up, using the thin-walled Kimble glass tubing previously mentioned (except for unit 84). These were studied for the effect of aging, speed of response, and temperature. The details of the construction of these units are given in table 2.

TABLE 2.—*Detail of construction of units*

Unit	Winding (tpi=turns of wire per inch)	Coated (1937)	Coating [1]	Remarks
KIMBLE SODA LIME GLASS TUBING, 17 MM DIAM, 0.5-MM WALL, GROUND-GLASS SURFACE				
84	16 tpi size 32 AWG tinned copper.	May 7	1 coat 1% LiCl	Outdoor exposure for 3 months.
KIMBLE FLINT GLASS, 10 MM DIAM, 0.3-MM WALL, SAND-BLASTED SURFACE				
101	16 tpi size 38 AWG copper.	June 24	1 coat 5% LiCl	Indoor exposure.
102	do	June 24	1 coat 10% LiCl	Do.
106	20 tpi size 38 AWG tinned copper.	June 26	1 coat 4% $ZnCl_2$; 1% of a 1.3 sp gr solution of H_2SO_4.	Do.
107	do	June 28	1 coat 4% LiCl, 4% $ZnCl_2$, 1% of a 1.3 sp gr solution of H_2SO_4.	Do.
108	do	June 28	1 coat 4% LiCl; 0.5% $LiNO_3$	Do.
113	16 tpi size 38 AWG tinned copper.	July 7	1 coat 10% LiCl; then coated with collodion and washed.	Washed after winding and coating. Indoor exposure.
114	do	July 7	1 coat 10% LiCl; then coated with balata dissolved in benzene; then washed.	Do.
118	20 tpi size 38 AWG tinned copper. Wound Oct. 8.	July 1	None	Indoor exposure.
119	20 tpi size 32 AWG tinned copper. Wound Oct. 8.	July 1	Powdered Corning 0.015 glass fused into surface of Kimble flint glass at 550° C; then washed.	Washed before winding; indoor exposure.
120	do	July 1	Powdered Li_2CO_3 fused on surface of flint glass at 550° C; then washed.	Do.

[1] Where percentage of coating is given, it refers to the percentage by volume of a saturated solution and water.

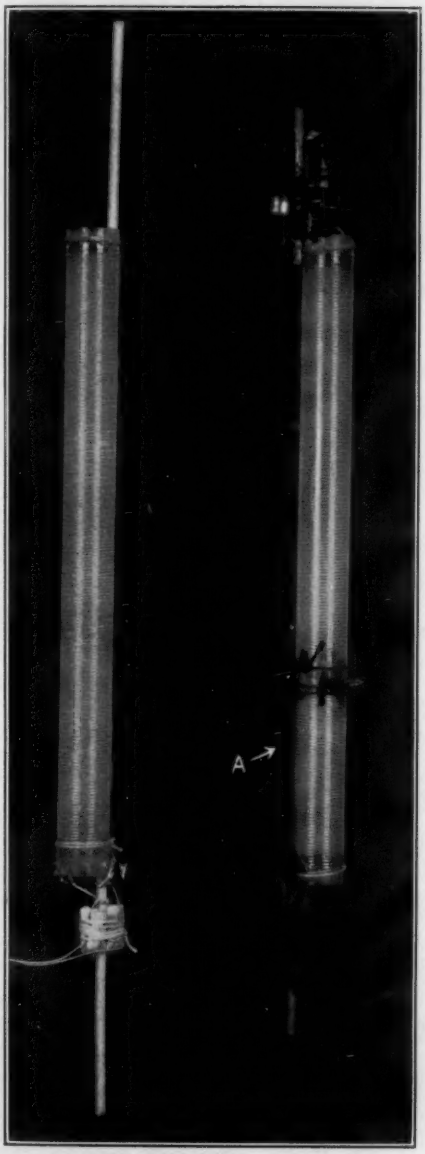


FIGURE 1.—*Final type of dual-coil hygrometer using thin-walled glass tubing, each coil having 20 turns per inch.*

The unit at the right has a temperature-operated range-expansion switch, shown at *A*.

1. EFFECT OF AGING

Figure 2 shows the effect of aging on the resistance of five of the Kimble flint-glass samples coated as indicated. The units were exposed to varying humidities during the interval from 0 to 160 days,

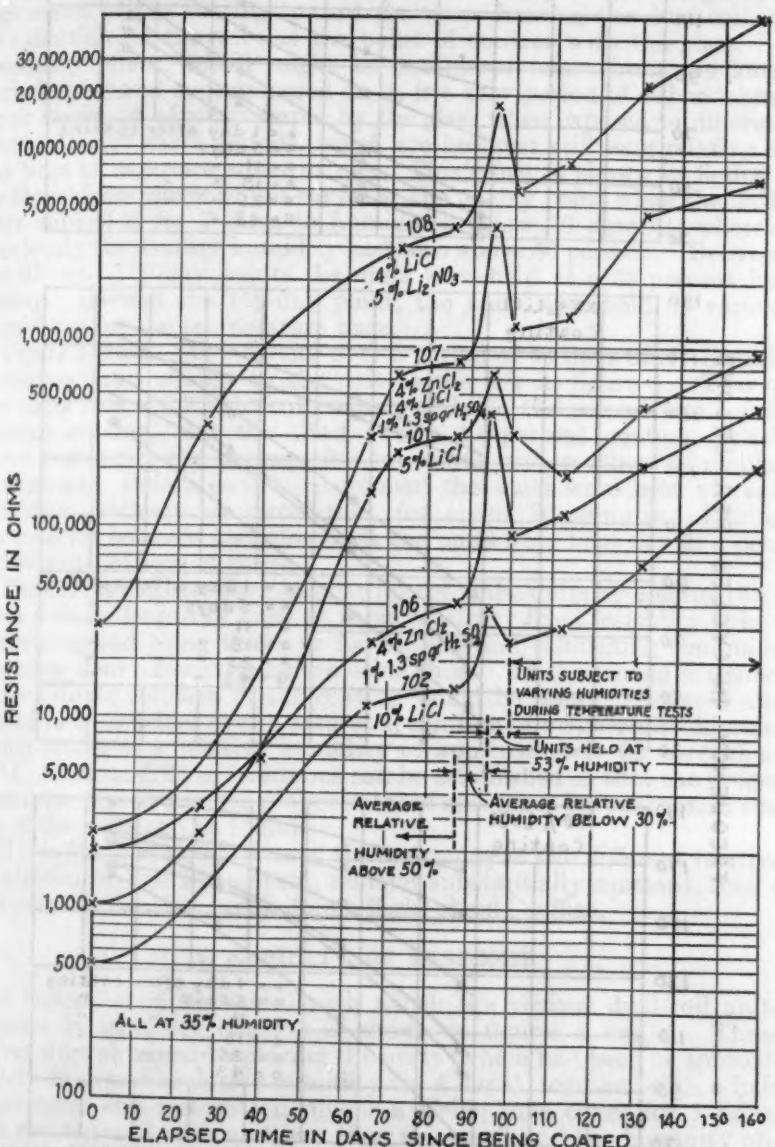


FIGURE 2.—*Effect of aging on the resistance at 35-percent relative humidity of five dual-coil hygrometers.*

but the measurements for the curves were always made after the units had been exposed to air of 35-percent humidity for several hours. The general increase in resistance indicates a long-period

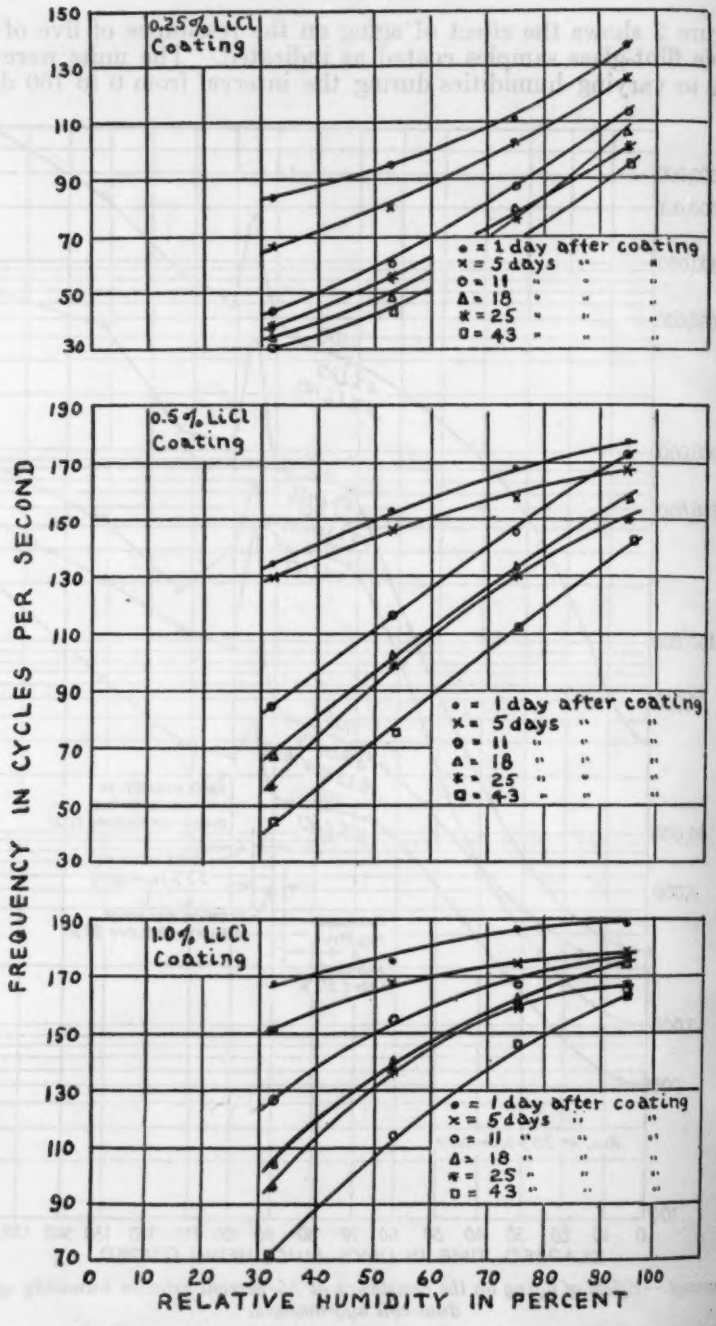


FIGURE 3.—*Effect of aging on dual-coil hygrometer units with different percentages of coatings of* LiCl.

aging phenomenon. Since all the units show the same general trend, i. e., resistance increase with time, the aging phenomenon might be due to a physical or chemical change in the exposed glass surface. It might be possible to find a more stable type of glass not subject to this phenomenon. The increase in resistance may be due to a gradual movement of the coating toward the wires forming the dual coil, or to oxidation on the wire at the point of contact with the glass. A secondary effect, which might be considered apart from the long-period aging and superimposed on it, is a slow period of either taking on or giving off of water vapor by the glass when exposed to different humidities for short periods, which are however still long relative to the time of exposure when in use. This effect is shown in figure 2 by the sudden jumps in the curves at the 95-day point when the units were subjected for 7 days to humidities below 30 percent, whereas previously the average humidity had been above 50 percent. Between the 95- and 100-day points the units were held at a 53-percent humidity. Beyond the 100-day point, the units were held at various humidities for the temperature tests.

Figure 3 shows the behavior over a period of 43 days of six Kimble flint-glass units similar to the unit at the left in figure 1. Two of the units had a 0.25-percent coating of LiCl, the second two a 0.5-percent coating, and the third two a 1.0-percent coating. Each curve represents the average for two units with coatings of similar percentage. Before each measurement the units were held at each humidity, without air circulation, for about 30 minutes. During the interval between measurements the units were kept dry in a container with calcium chloride.

The curves indicate the necessity for aging the units by holding them for a definite length of time at some arbitrary fixed humidity before calibrating and using them, or for coating and calibrating the units, not more than a few days before using them. In the second instance, a more dilute solution of the coating would be used. If coated and placed in a container over a saturated solution of magnesium chloride, which produces a relative humidity of approximately 32 percent at 24° C, the true drift in resistance can be established so that the proper time corresponding to the proper value of resistance for calibration and use of the units can be found.

If it is found that the ratio of the resistance at two different relative humidities, 45 and 100 percent, remains substantially constant, then a one-point calibration just before a flight should suffice.

2. RAPIDITY OF RESPONSE

An indication of the speed with which the various dual-coil units respond to humidity changes is shown in figures 4 and 5. These curves were obtained by placing the units (which had been at approximately 50 percent relative humidity for 4 days), together with a hair hygrometer and wet cotton, under a Cellophane cover for 1 hour. The resistance of each unit was then measured and the humidity obtained from previous calibrations. The average humidity indication for all 10 units was 68 percent. The hair hygrometer read 65 percent. The covering and wet cotton were then removed and air at the room humidity of 28 percent was circulated at a rate of approximately 150 ft per minute over the hair hygrometer and all of the units. Their resistances were measured (as rapidly as possible at first) for a period

of 50 minutes. The curves of figures 4 and 5 show the results. It will be noted that even with this low air velocity (normal balloon ascent rate is 600 ft per min), sample 101 (coated with 5 percent LiCl) indicated a drop from 68-percent relative humidity to 32 percent (28 percent being the final value) within 40 seconds. Other units responded with varying speeds depending upon their makeup.

The hair hygrometer was more sluggish than any of the units. The slow response of the hair hygrometer, as compared with unit 101, for

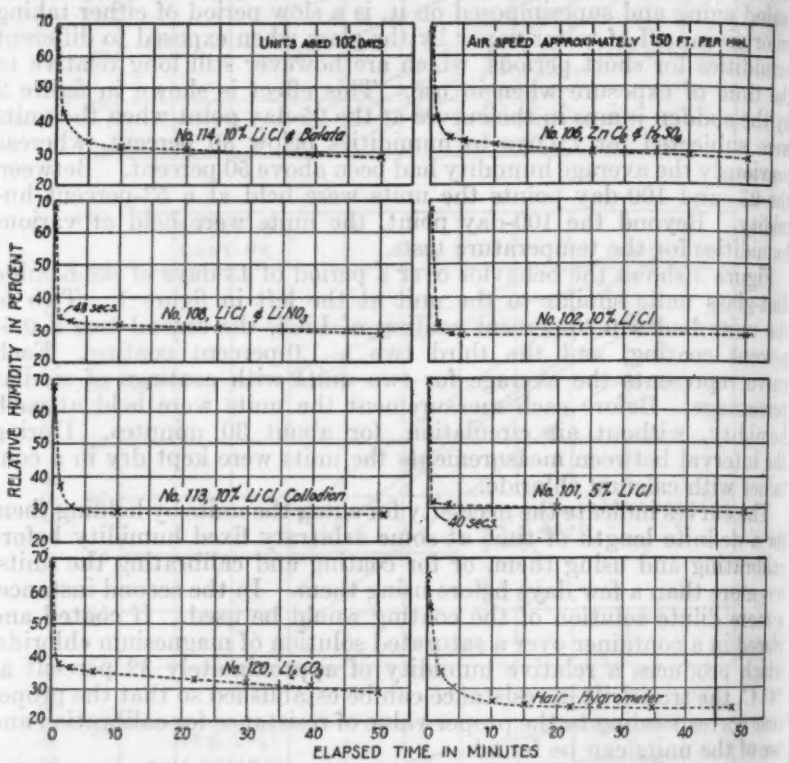

UNITS AGED 102 DAYS
AIR SPEED APPROXIMATELY 150 FT. PER MIN.
No. 114, 10% LiCl & Bakelite
No. 106, $ZnCl_2$ & H_2SO_4
48 secs.
No. 108, LiCl & $LiNO_3$
No. 102, 10% LiCl
No. 113, 10% LiCl, Collodion
No. 101, 5% LiCl
40 secs.
No. 120, Li_2CO_3
Hair Hygrometer
RELATIVE HUMIDITY IN PERCENT
ELAPSED TIME IN MINUTES

FIGURE 4.—*Relative speed of response of seven different dual-coil hygrometers and a hair hygrometer at 24° C when taken from a 68 percent humidity chamber and placed in a 28 percent humidity air-stream flowing at 150 ft per minute.*

example, may best be seen in figure 5. Here the abscissas represent elapsed time. The ordinates represent percent error in terms of the final value of 28-percent relative humidity. In 30 seconds, sample 101 read within 15 percent of the true humidity while the hair unit was 65 percent in error. These results indicate an approximate time-lag constant of 4.5 seconds in an air stream of 150 ft per minute for glass hygrometer unit 101, as compared with 42 seconds for the hair hygrometer. The capillary-tube electrolytic thermometer has a time-lag constant approximately equal to that of the glass hygrometer. From the standpoint of time lag, it is clearly evident that the dual-coil hygrometer is far superior to the hair-type hygrometer in giving a truer picture of the humidity structure of the upper atmosphere when used on a rapidly ascending balloon.

The relative rapidity with which the various units took on water vapor when the moist cotton was put into the Cellophane container with them, is shown in the curves in figure 6. These curves do not indicate the true rate of response, as the humidity was gradually increasing from 35 to 63 percent during the hour indicated. Also, there was no air circulation in the chamber.

While unit 108 (LiCl and $LiNO_3$) seems to respond to the absorption of water most rapidly, its curve for giving up water vapor (see fig. 4) shows considerable lag. From the point of view of quick response both with respect to taking on and giving off water vapor, sample 101

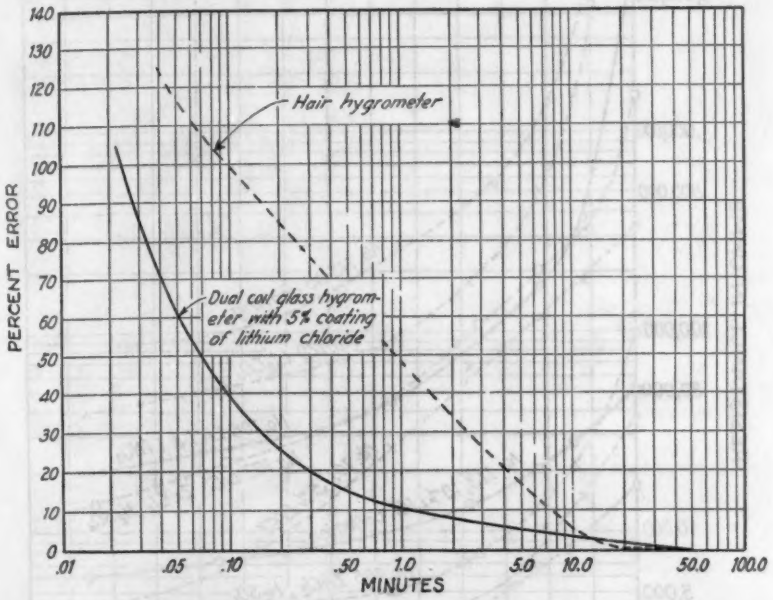


FIGURE 5.—*Percentage error due to lag in response of the hair hygrometer as compared with a 100-day-old dual-coil unit with a 5 percent* LiCl *coating at 24° C, when taken from a 68 percent humidity chamber and placed in a 28-percent humidity air-stream flowing at 150 ft per minute.*

(5 percent LiCl) seems the best. Experience shows that all units tend to respond more rapidly to an increase in humidity than to a corresponding decrease. The curves in figure 6 should not be compared with those in figure 4, for the reasons mentioned.

3. DETERMINATION OF TEMPERATURE CORRECTION

Through the cooperation of the Bureau's aeronautic instrument section, a study of the effect of temperature on the operation of the dual-coil glass hygrometer was made. The 11 units which had been coated for about 100 days were put into an airtight chamber with a large pan full of certain salts partially dissolved in water. The humidity produced at different temperatures by each of these four salts used separately in the airtight chamber had been previously determined. Before making the set of humidity-temperature measurements, the units were held at 53 percent relative humidity and 25° C for 4 days. With each salt in the chamber the resistance

readings of each unit were taken at +30, +15, and 0° C; and at −10 and −20° C with two salts, giving approximate humidities of 88 and 50 percent at −10° C, and 87 and 54 percent at −20° C. The chamber was held for 1 hour at each new temperature before measuring the resistance of the units. During the interval overnight when not under test, the units were held at 15 to 20° C and at the humidity to be used next. The temperature runs were made with the different

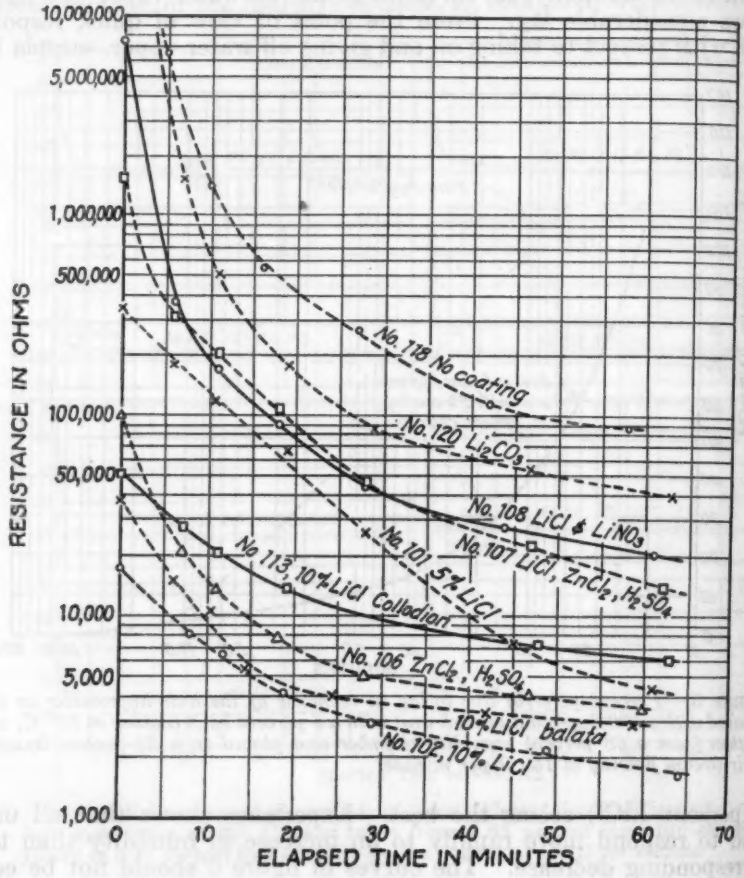


FIGURE 6.—*Relative water-vapor adsorption characteristics of differently coated dual-coil hygrometers.*

humidities in the following order: 53, 75, 94, 33, and 87 percent. Between the 94-percent run and the 33-percent run, the samples were left for 2½ days at 33 percent and 30° C.

The curves in figures 7 and 8 represent the results of these tests. The results for units 84 and 119 are omitted as these showed an erratic behavior. The curves for unit 120 are also omitted as they were quite similar to those for unit 108. Up to the time of writing this paper, measurements below 54-percent humidity at temperatures of −20° C or below had not been made, as salts for establishing low humidities at low temperatures had not been calibrated. From the trend of the curves and from flight tests, the indications are that these

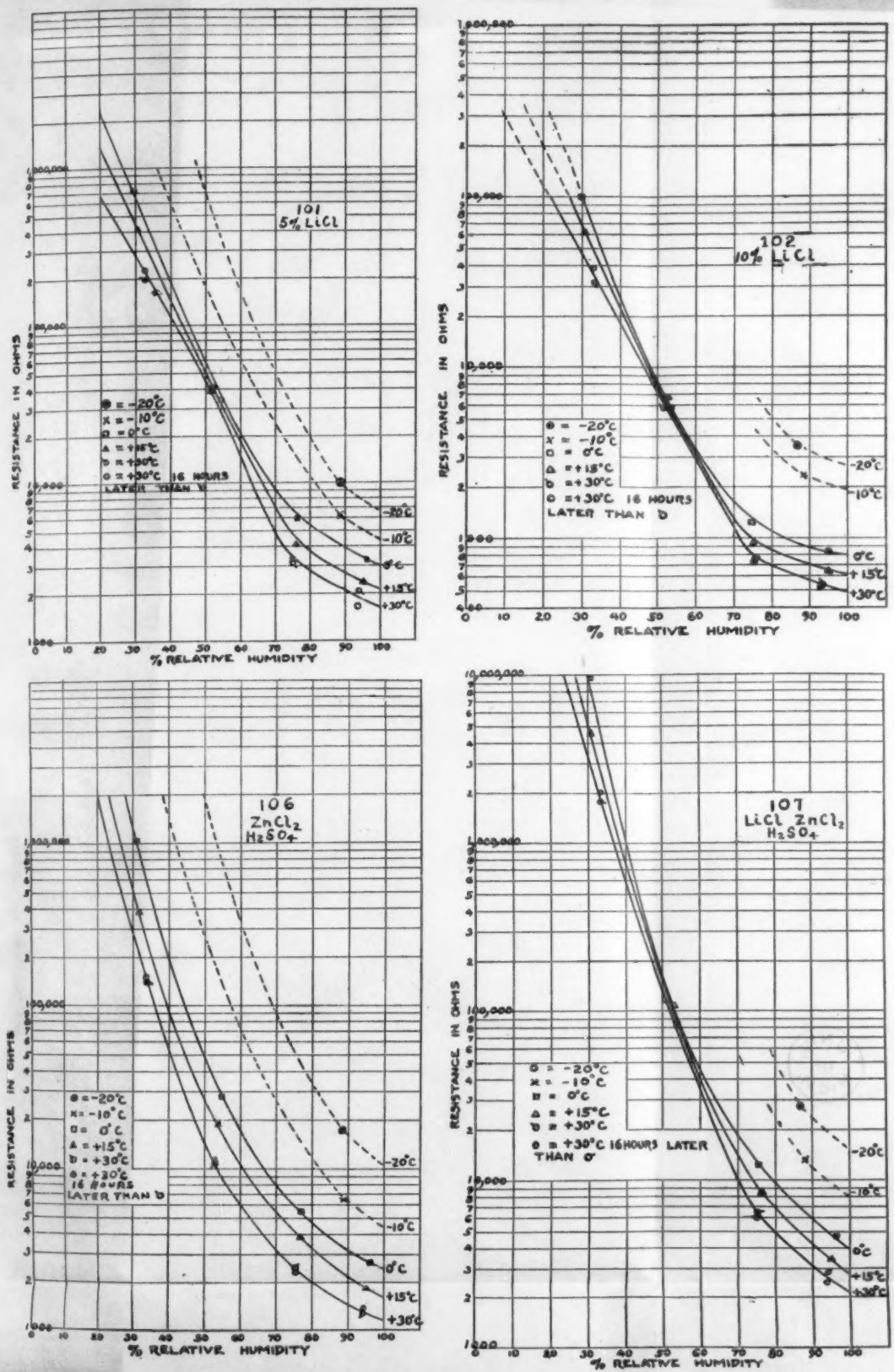
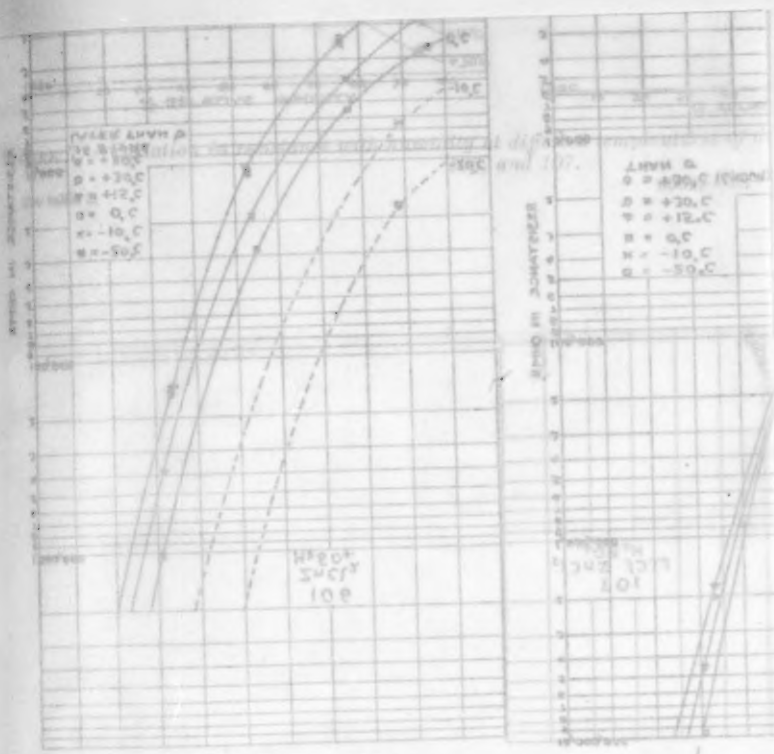
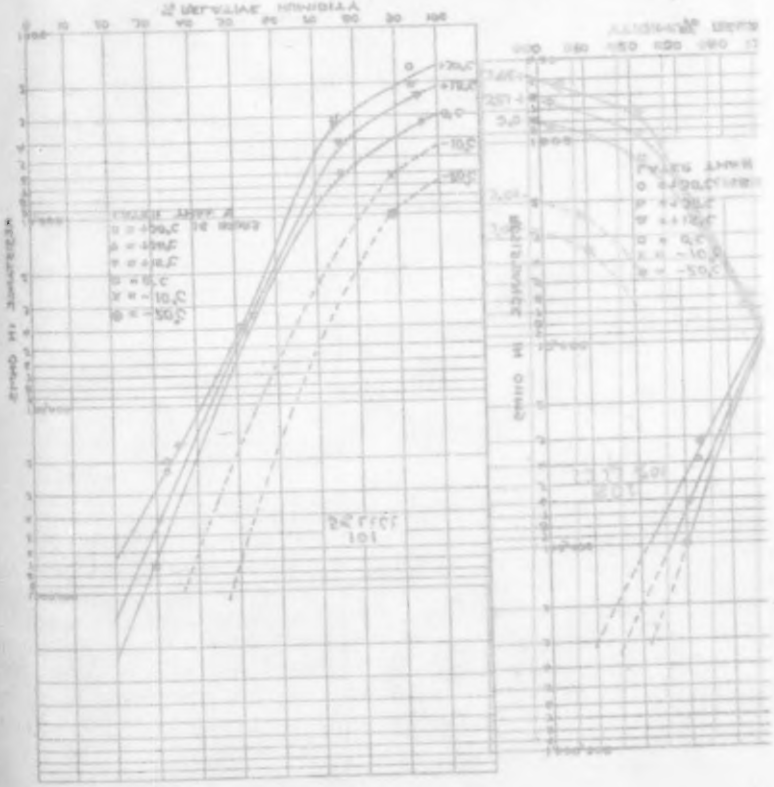
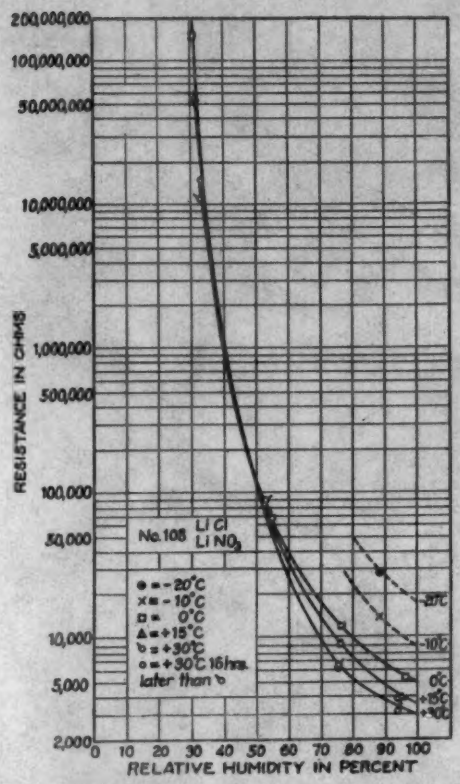


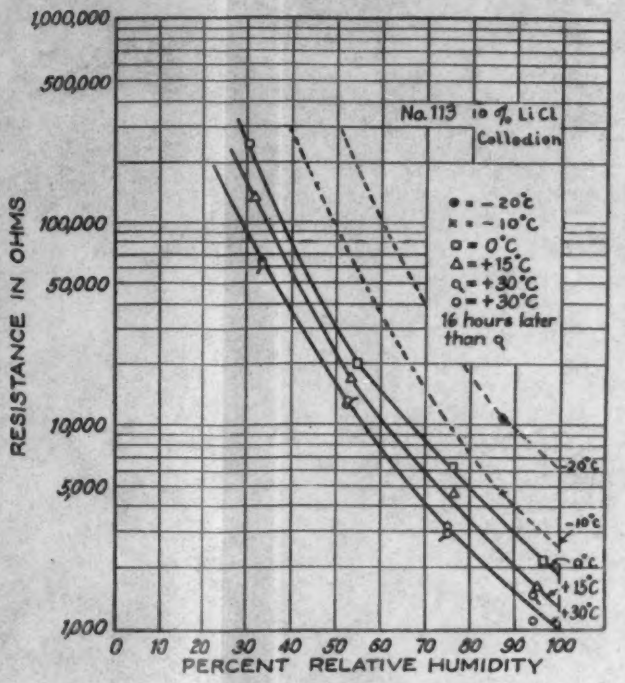
FIGURE 7.—*Variation in resistance with humidity at different temperatures of dual-coil hygrometers 101, 102, 106, and 107.*

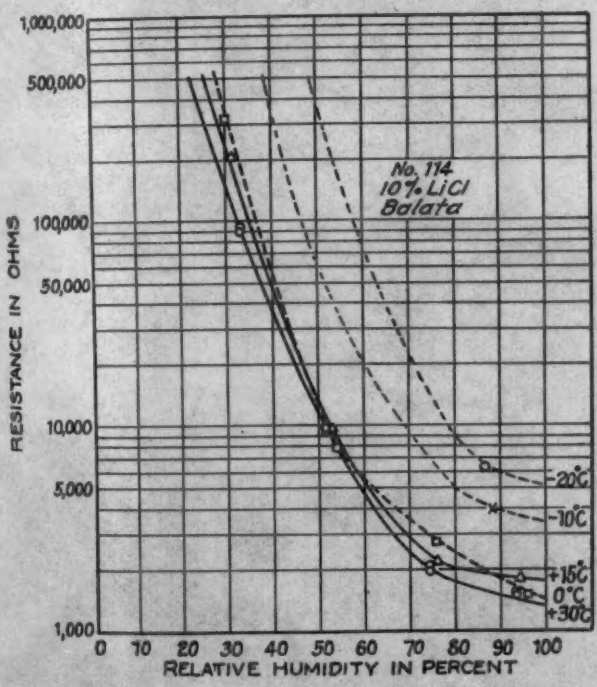
See table 2.











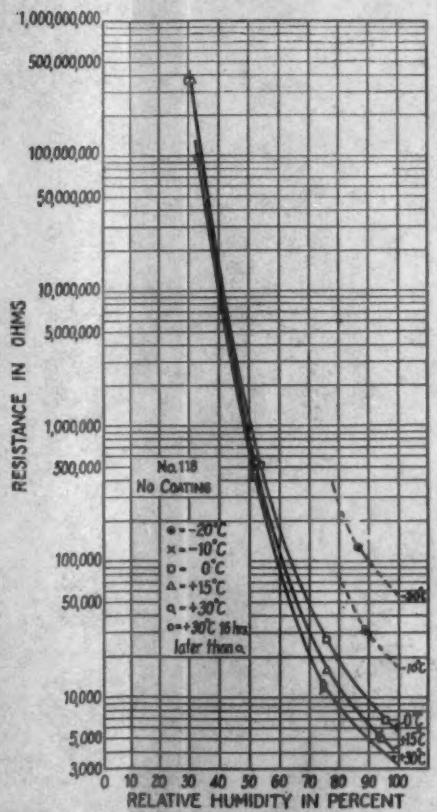


FIGURE 8.—*Variation in resistance with humidity at different temperatures of dual-coil hygrometers 108, 113, 114, and 118.*

See table 2.

RESISTANCE IN OHMS
RELATIVE HUMIDITY IN PERCENT
0
10
20
30
40
50
60
70
80
90
100
1,000
5,000
10,000
50,000
100,000
500,000
1,000,000

units continue to function down to stratosphere temperatures. From figures 7 and 8 it will be noted that temperature correction is greater for some of these units than for others and varies with the humidity.

The effect of temperature at 90-percent relative humidity is shown in figure 9. In this figure the full line represents the average error in indicated values of relative humidity when using the +30° calibration. The average is for units 101, 102, 107, 108, 113, 118, and 120. The dotted lines represent the maximum deviation above and below this average. The greatest deviation is about 9-percent relative humidity. The above units were all different, having various types of windings and coatings. It is to be expected that had the above seven units been identical in construction, each with a coating of, say, 5 percent LiCl, and had they been aged the same length of time, that the maximum deviation would have been less than 3 percent. The data in

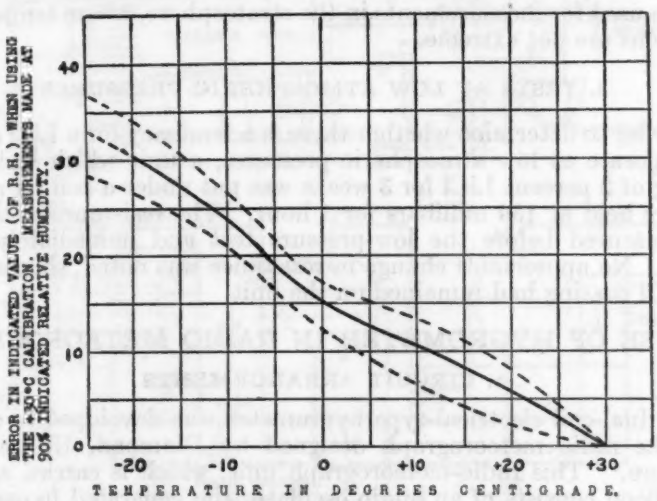


FIGURE 9.—*Average deviation in percentage relative humidity (figs. 7 and 8) of the indicated humidity readings (based on a +30° C calibration) from the true 90-percent value of relative humidity for units 101, 102, 107, 108, 113, 118, and 120.*

figures 7, 8, and 9 would indicate that it should be possible to establish the proper temperature-correction factor for a standardized design of unit which should apply to all units similarly constructed. A check at three or four humidities at room temperature should then be sufficient. Any deviation from normal at room temperature in this check could be applied throughout the temperature range.

In radio meteorography it is customary to measure temperature when measuring humidity, so the proper temperature curve of the family of humidity-resistance curves may be used to obtain the true relative humidity.

From the data shown in figures 7 and 8 it would appear that a good unit would be one similar in mechanical construction to unit 118, i. e., one having a winding of 20 dual turns per inch of size 36 or 38 AWG tinned copper wire. The coating should be LiCl, unless further measurements at temperatures below −20° C show some of the other coatings to be superior. The percentage strength of LiCl to be used for coating each unit will be dependent upon the aging period

adopted, the temperature range to be covered, the method of applying the coating, and the portion of the humidity scale of most interest. In all cases the coatings were applied with a camel's-hair brush, using just enough of the liquid mixture to moisten the glass surface. If two units are to be used and are coated a day or so before use, a good coating is 0.25 percent LiCl on one unit and 1.0 percent on the other. A coating of 0.5 percent gives a good range of resistance variation from 0- to 100-percent humidity at temperatures down to −15 or −20° C.

It has been noted when testing freshly coated units between 0 and +30° C, that the change in resistance with humidity relative to the change due to temperature is greater the less the percentage of LiCl. Thus an uncoated unit is least affected (relatively) by temperature change, while a unit freshly coated with 3 percent LiCl or more has a marked temperature correction. A 3-percent unit would, however, only be used for measurements in the stratosphere, where temperature variations are not extreme.

4. TESTS AT LOW ATMOSPHERIC PRESSURES

In order to determine whether there is a tendency for a LiCl coating to evaporate at low atmospheric pressures, a unit which had had a coating of 2 percent LiCl for 3 weeks was put under a bell jar and the pressure held at 159 millibars for 1 hour. The resistance of the unit was measured before the low-pressure test and immediately afterwards. No appreciable change in resistance was noted, showing that the LiCl coating had remained on the unit.

VI. USE OF HYGROMETER IN RADIO METEOROGRAPH

1. CIRCUIT ARRANGEMENTS

The dual-coil electrical-type hygrometer was developed to operate with the radio meteorograph designed by Diamond, Hinman, and Dunmore.[4] This radio-meteorograph unit, which is carried aloft by the balloon consists of an audio oscillator the generated frequency of which is a function of the resistance across the input grid and filament. This resistance is made up of the electrolytic thermometer, hair-controlled resistor, or photoelectric cell. The audio frequency produced by the variation in resistance of each of these units is a function of the phenomenon they are measuring.

A circuit arrangement (described in reference 2) for adapting the dual-coil hygrometers to the radio meteorograph is shown in figure 10. In this circuit, one or more dual-coil hygrometers may be successively connected to the relaxation-oscillator input circuit in addition to the other measuring devices. A motor- or fan-operated switch serves to make the necessary connections so that each measurement is transmitted three times a minute or faster.

The usable range of resistance variation of any unit is limited by the fact that the relaxation oscillator will not function properly with less than 40,000 ohms across its input. The relaxation-oscillator circuit is so adjusted that this value of resistance produces a frequency of 200 cycles, which is the upper scale limit of the audio-frequency meter used at the receiving station. The lower limit used on the frequency meter is 20 cycles. The relaxation oscillator is limited to this lower frequency by shunting its input with a fixed resistor of

[4] J. Research NBS 20, 369 (1938) RP1082.

350,000 ohms. These limitations require the use of two units in order to measure humidities at temperatures as low as −70° C, as the resistance of a unit designed to work at the higher temperatures would become too high at low temperatures to function in this circuit.

Figure 11 shows the variation of the relaxation-oscillator frequency as a function of the resistance of the dual-coil hygrometer or other device. The grid-circuit resistance consists of the device with 40,000 ohms in series and 350,000 ohms in shunt. In this figure, R_H is the hygrometer unit and R_o is the resultant resistance across the input terminals A and B of the relaxation oscillator. From figure 11 it will be seen that the actual usable range of variation of resistor R_H is from

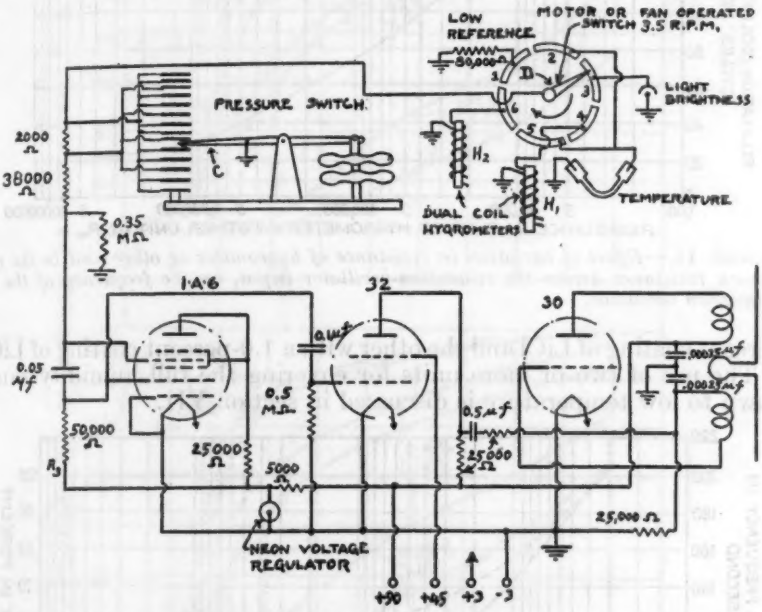


FIGURE 10.—*Radio-meteorograph circuit arrangement, showing pressure-shorting switch and motor-operated selector switch for six different measurements.*

about 3,500 ohms to 4.0 megohms. Since the resistance of R_H does not vary linearly with humidity, figure 11 does not give the relationship for converting humidity into frequency. Data for converting humidity into frequency variations are shown in figure 12. The lower curve shows the effect on the frequency of the relaxation oscillator when a unit varies in resistance from 3,500 ohms to 4 megohms. For a unit with a very small percentage of the LiCl coating, this might correspond, as shown by the upper curve, to a change in humidity at 30° C, from 100 to 45 percent.

In figure 13 is shown the results of frequency measurements with dual-coil units having different percentages of the LiCl coatings, and used in the standard radio-meteorograph circuit shown in figure 10. The measurements at 24° C (lower set of graphs) were made the day after coating, and those at 0° C (upper set of graphs) were made 3 days after coating. From the trend (due to temperature) of these curves, it appears that a 0.5-percent coating should give good humidity

indications from +24° C to approximately −20° C. In order to cover the full temperature range (+30° C to −70° C) it would appear from these graphs that two units should be used, one having a 0.25-

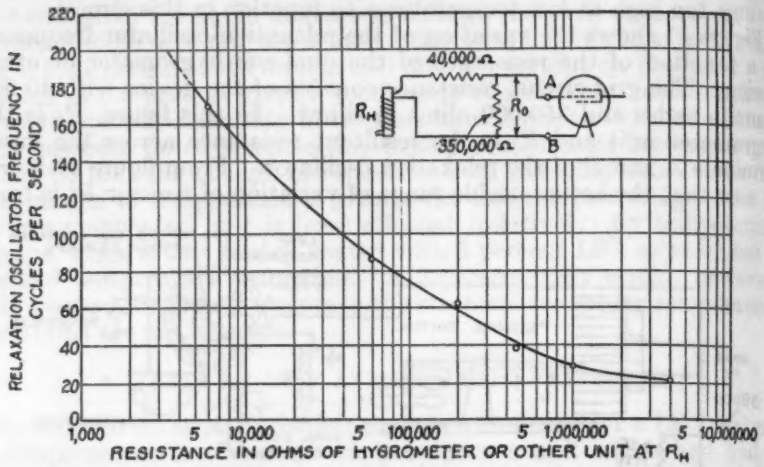


FIGURE 11.—*Effect of variation in resistance of hygrometer or other unit in the network resistance across the relaxation-oscillator input, on the frequency of the relaxation oscillator.*

percent coating of LiCl and the other with a 1.0-percent coating of LiCl.

The use of two or more units for covering the full humidity range down to low temperature is discussed in section VII.

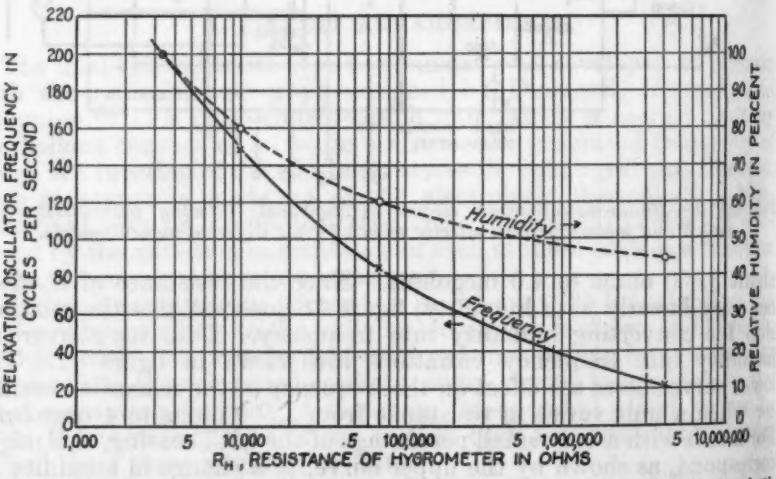


FIGURE 12.—*Variation of relaxation-oscillator frequency as a function of the resistance of a hygrometer unit at R_H in the circuit network shown in figure 11.*

Referring again to figure 10, the lower half of the figure represents the relaxation oscillator, modulation amplifier, and 65-megacycle oscillator with doublet antenna. The pressure- and motor-switching units are shown above. The circuit is such that when arm *C* of the atmospheric pressure-operated switch is on an insulated segment, the rotation of arm *D* of the motor-operated switch serves to connect the

various measuring units to the input of the relaxation oscillator with the 38,000 and 2,000 ohms (40,000) in series and the 350,000 ohms in shunt. As the balloon rises from the ground, arm *C* first contacts the top No. 1 conducting segment of the pressure switch and all of the measuring units are shorted, leaving the 38,000 and 2,000-ohm resistors

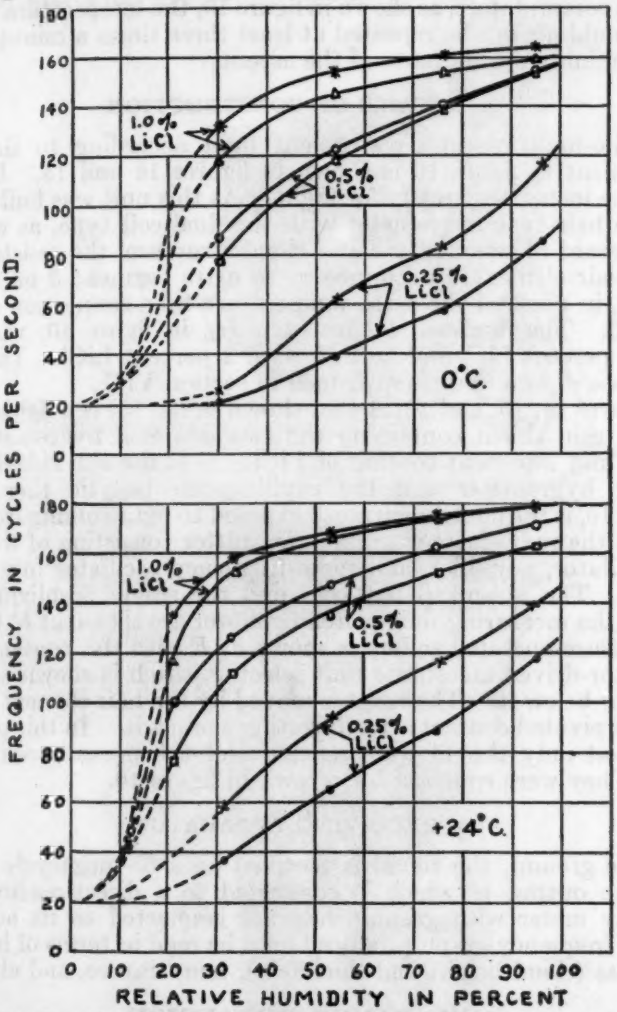


FIGURE 13.—*Humidity-frequency characteristics at 0° C and +24° C for dual-coil units with different percentages of* LiCl *coatings.*

in series across the input to the relaxation oscillator. This is the case for segments 1 and 2, 4 and 5, 7 and 8, etc. This fixes definite altitude points and gives a check on the relaxation-oscillator frequency calibration at the high end of the range. When arm *C* touches conducting segments 3, 6, 9, etc., counting from the top, a slightly different note is transmitted, as the 38,000-ohm resistor only is thrown into circuit. This change in note facilitates contact identification. The conducting segments are much narrower than the insulated segments so that the recording units are shorted out of circuit for as small a percentage of

the time as possible—something like 15 percent, depending upon the segment width and number of conducting segments used. If each of six effects is transmitted three times a minute, the loss of a measurement of one or two of the effects for half a minute in each two or three minutes is not serious. If the temperature unit is connected to two opposite commutators, as shown in figure 10, the temperature measurement should always be repeated at least three times a minute and six times a minute during parts of the ascent.

2. DETAILS OF CONSTRUCTION

A radio-meteorograph instrument built according to the circuit arrangement in figure 10 is shown in figures 14 and 15. Figure 16 shows the instrument ready for flight. As this unit was built to compare the hair-type hygrometer with the dual-coil type, as well as to give a record of temperature and cloud structure, the resistor varied by the hair element was connected to extra segment 5 on the commutator, in place of the extra temperature tube connection shown in figure 10. The dual-coil hygrometer, H_1, in figure 10, was coated with 0.5 percent LiCl and unit H_2 with 2 percent LiCl. The reason for the use of two units is explained in section VIII.

In figures 14, 15, and 16, A (not shown in fig. 15) is a double-walled sun and rain shield containing the two dual-coil hygrometers with the 0.5- and 2-percent coating of LiCl. B is the sun shield housing the hair hygrometer and the capillary electrolytic thermometer. G, figure 16, is the photoelectric cell exposed to light coming from below it. D is the radio-meteorograph transmitter consisting of the relaxation-oscillator, amplifier, and radio-frequency oscillator in a shielded housing. The A and B batteries and the single flashlight cell for running the measuring unit switching motor are shown at E, figure 14. The pressure-operated switch is shown at F with the contact arm C. The motor-driven measuring unit selector switch is shown at H with the motor below it. The resistor moved by the hair element is shown at I with pivoted contact arm, J, resting against it. In this particular instrument only the 14 wide segments of the pressure switch were used. They were connected as shown in figure 10.

3. RECEIVING APPARATUS

On the ground, the signal is received on a 65-megacycle receiver, the audio output of which is connected to a direct-reading audio-frequency meter with graphic recorder connected to its output, so that the frequency graph produced may be read in terms of humidity, brightness (cloud height and thickness), temperature, and altitude.

VII. RANGE EXPANSION

An advantage of this electrical-type hygrometer, not possible with the hair unit, is the ability to expand the humidity scale by the use of two or more units of different sensitivity, each coated to vary over approximately the same resistance range but within different temperature ranges. The extra units may be switched into circuit by a bimetallic temperature-operated switch or by a pressure-operated switch, after the unit has reached a certain low-temperature point or a certain altitude. A temperature-switched unit is shown at the right in figure 1. The bimetallic strip shown at A short-circuits the lower insensitive portion of the unit when a temperature of −20 or

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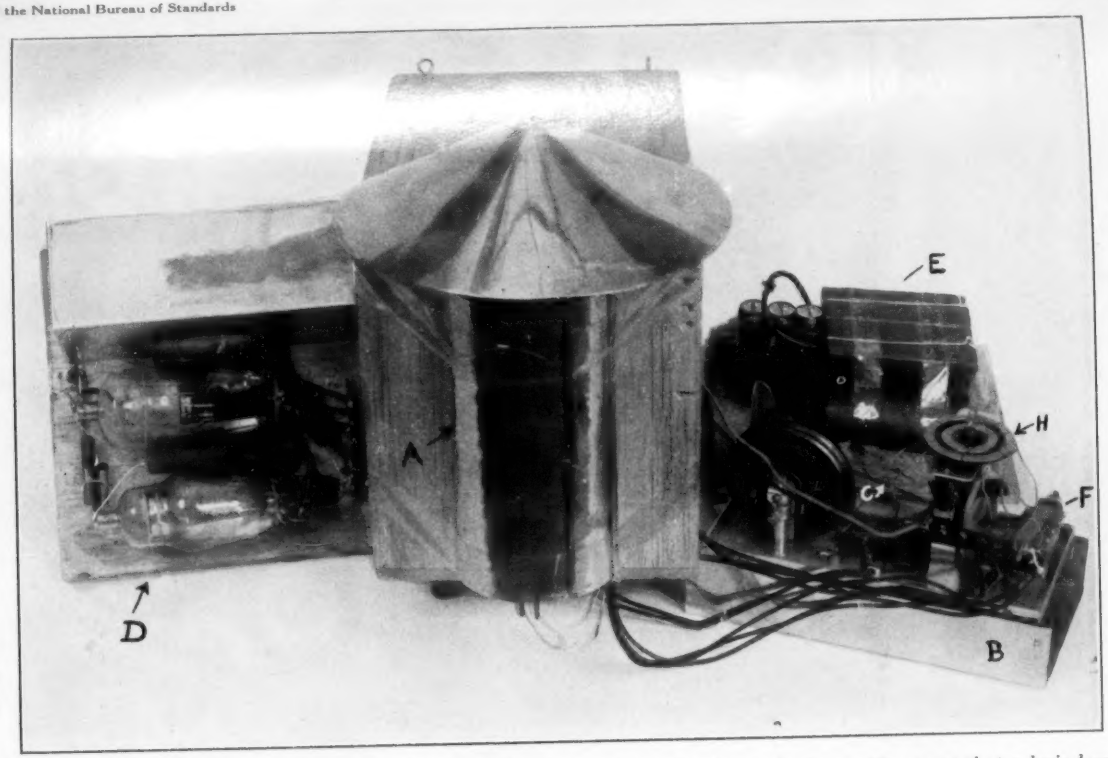


FIGURE 14.—*The radio meteorograph constructed according to the circuit arrangement shown in figure 10, except that a hair-hygrometer operated resistor was connected to the extra electrolytic-thermometer segment.*

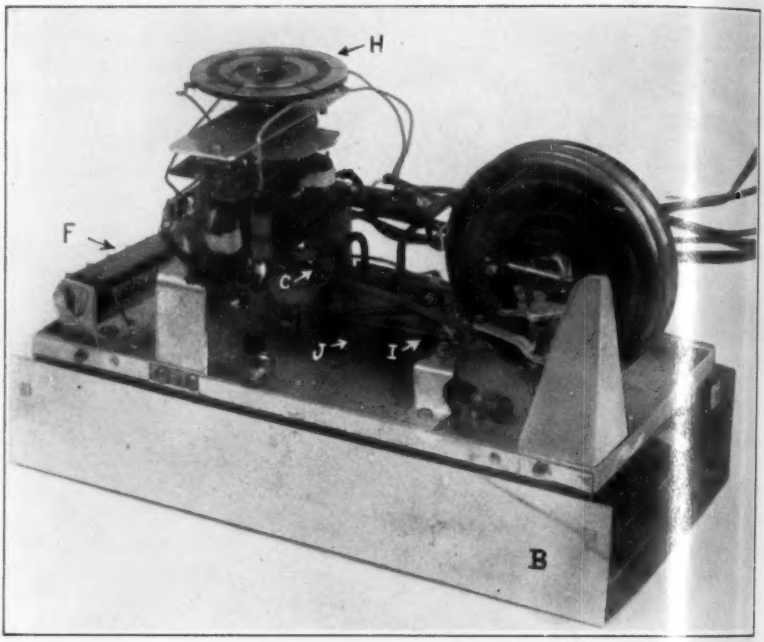


FIGURE 15.—*The radio-meteorograph pressure-operated switch for giving altitude, and motor-operated selector switch for connecting each of the six different measuring units for 3.5 seconds to the relaxation oscillator.*

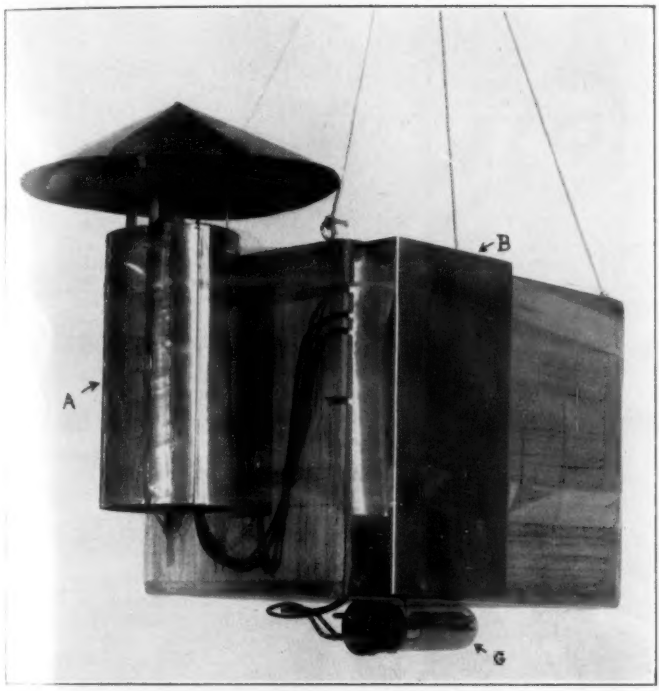


FIGURE 16.—*The multi-purpose radio meteorograph ready for use.*

This unit contains an electrolytic thermometer, hair-hygrometer operated resistor, two dual-coil hygrometers, and a photoelectric cell.

−30° C is reached. The resistors at the top are in shunt with the upper coil section and serve to indicate when the temperature switch closes, should it close when the resistance of both sections is extremely high. Another method of switching two different humidity units into circuit would be to use a simple single-pole double-throw relay-operated switch, the relay being caused to function by a circuit of proper time constant. In cases where a motor-, fan-, or clock-operated switch is used as described under section VI, to throw the temperature-, pressure-, and light-intensity measuring units into the relaxation-oscillator circuit, a number of extra contacts on the commutator may by provided, for as many humidity units as desired. As the measurement of temperature, humidity, etc., is not a function of the speed of

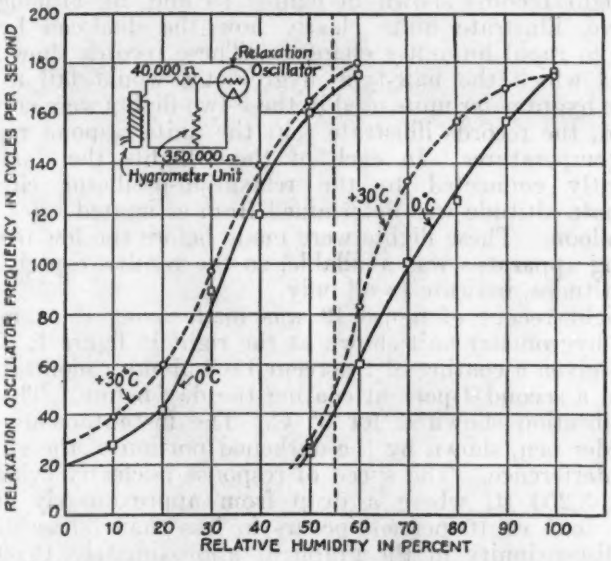


FIGURE 17.—*Variation in frequency of the relaxation oscillator as a function of humidity and temperature, showing use of two dual-coil hygrometers with different percentage of LiCl coating, for range expansion.*

the switching motor, it is not necessary to use a motor of constant speed, which reduces the cost of the motor.

One humidity unit may be designed and calibrated to give nearly full-range coverage on the receiving graphic-frequency recorder for the whole humidity range for temperatures between +30 and −10° C, while a second unit with more turns and a higher percentage coating of the LiCl or other coating may be made to give the same coverage on the recorder for the whole humidity range for temperatures between −10 and −40° C, and a third unit, if desired, coated to cover the humidity range at temperatures from −40 to −70° C. Or it may be found possible with the proper choice of coatings, as mentioned in section VI, to use two units, one for temperatures from +30 to −30° C and the other from −30 to −70° C.

For high sensitivity, where one is concerned only with a total temperature range of 40° C or less, two units may be made to cover the full humidity scale. One unit might cover 0- to 50-percent humidity and the other 50 to 100 percent. Two such families of frequency-humidity curves are shown in figure 17, the curves at the

left being for a unit with a higher percentage of LiCl than those at the right.

In figure 18 are shown two humidity units mounted in a double shield for protection against the sun's heat and from direct rain. It is important in recording relative humidity that the glass hygrometer unit be at the same temperature as the air, the humidity of which is to be measured. This is the reason for using a glass tube with a wall thickness of only 0.3 mm and for constructing and mounting the tube so that the air may circulate over both of the inside and outside wall.

VIII. FLIGHT TESTS

The flight records shown in figures 19 and 20, although purely qualitative, illustrate quite clearly how the dual-coil hygrometer responds to rapid humidity changes. These records show humidity variations which the hair-type hygrometer would fail to register. While the hygrometer units used in these two flights were only roughly calibrated, the records illustrate that the units respond rapidly and at low temperatures. In each of these flights the dual-coil was permanently connected to the relaxation-oscillator circuit, and approximate altitude was determined from estimated rates of ascent of the balloon. These flights were made before the low-temperature calibrating apparatus was available, so the results, especially at the higher altitudes, indicate trend only.

The flight record of figure 19 was made using the temperature-switched hygrometer unit shown at the right in figure 1. This unit had been given a coating of 1 percent LiCl about a month before the flight and a second 1-percent coating the day before. The approximate calibration shown is for 0° C. The instantaneous jumps of the recorder pen, shown by the darkened portion of the graph, were due to interference. The speed of response is clearly evident, especially at 3,200 ft, where a drop from approximately 40-percent humidity to 5 or 10 percent occurs in less than 30 seconds. The sudden discontinuity in the graph at approximately 18,600 ft was caused by the temperature switch closing and thereby allowing the more sensitive portion of the hygrometer unit to function and show humidity variations up to 43,000 ft and above. Note the fine structure of the humidity variations, especially at 9,800 ft.

On January 18, 1938, the sky being overcast, a flight was made, using the radio meteorograph shown in figures 14 to 16. 2¼ hours later a second flight was made, using a similar unit. The ascent rates were about 1,100 feet per minute. The circuit arrangement was that shown in figure 10, except that a hair-hygrometer unit was connected to segment 5 in place of the second temperature tube connection. In these flights the arm, D, of the six-segment commutator, figure 10, rotated at about 3.5 rpm. Each effect was therefore transmitted for about 3 seconds on an average of 3.5 times per minute. The dual-coil hygrometer unit, H_1, was coated with 0.5 percent LiCl and unit H_2 with a 2.0-percent coating. Each was coated the day before using. The graph shown in figure 21 is a photographic copy (reduced in size) of the actual first-flight record, as traced by the graphic frequency recorder at the receiving station. The full- and dotted-line traces of the envelopes of temperature, light, and three humidity records, were added to make the record more intelligible. In this graph the short dotted line is a record of brightness as received from

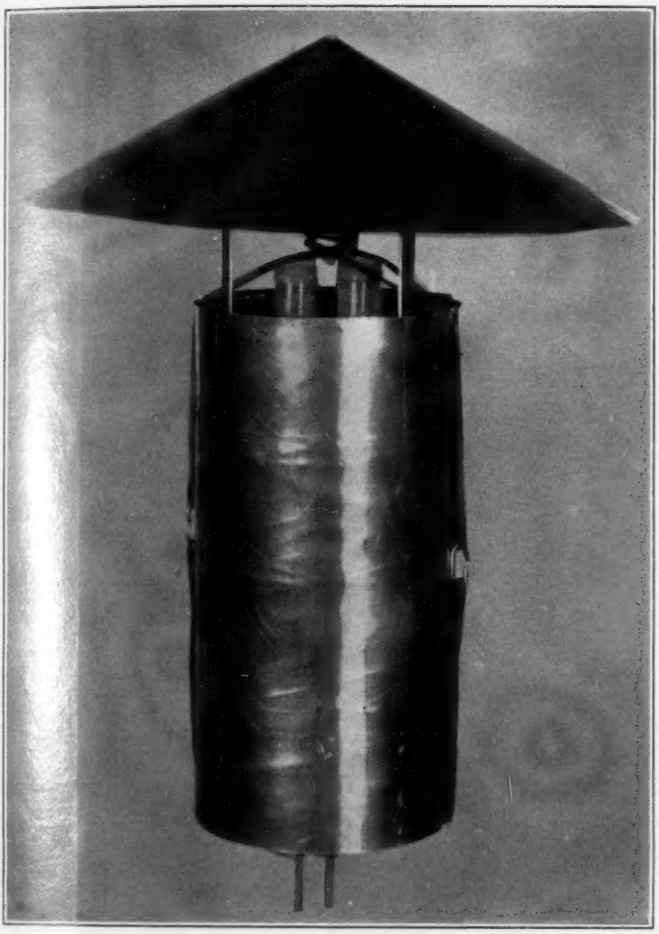


FIGURE 18.—*Double-walled sun and rain shield housing for two dual-coil hygrometers.*

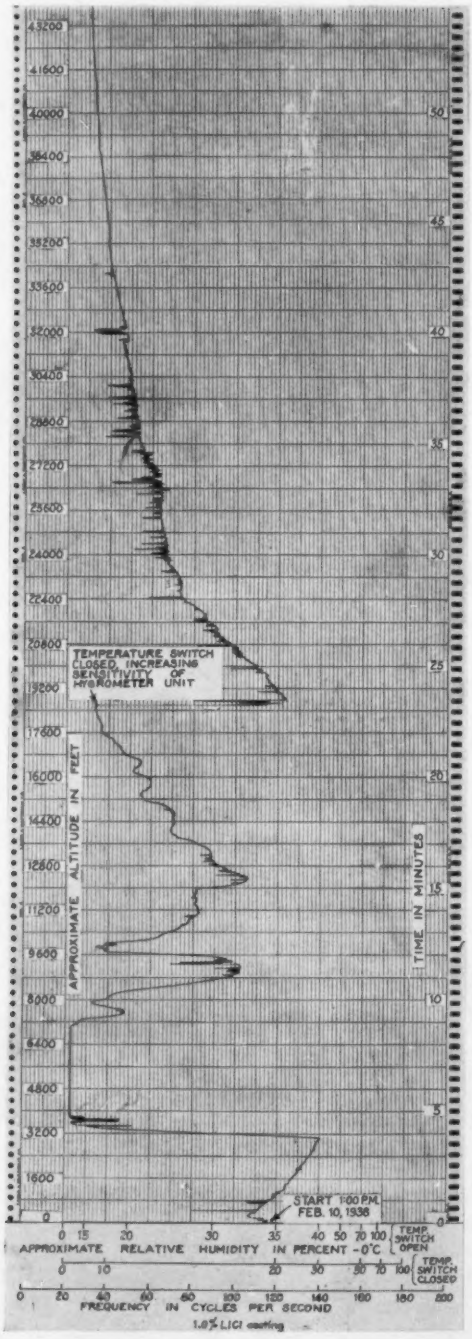


FIGURE 19.—*Humidity flight record using the dual-coil* LiCl *coated hygrometer, with temperature switch shown in figure 1.*

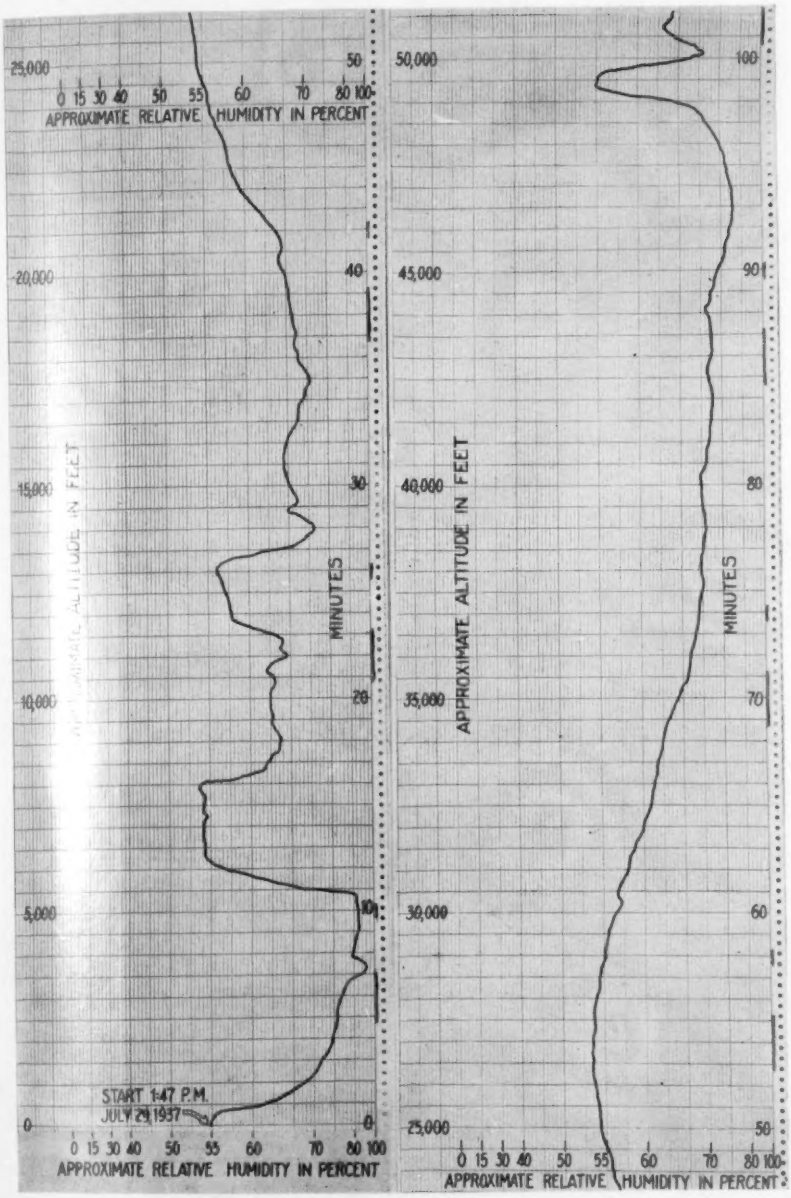


FIGURE 20.—*Humidity flight record using dual-coil hygrometer showing response at high altitudes.*

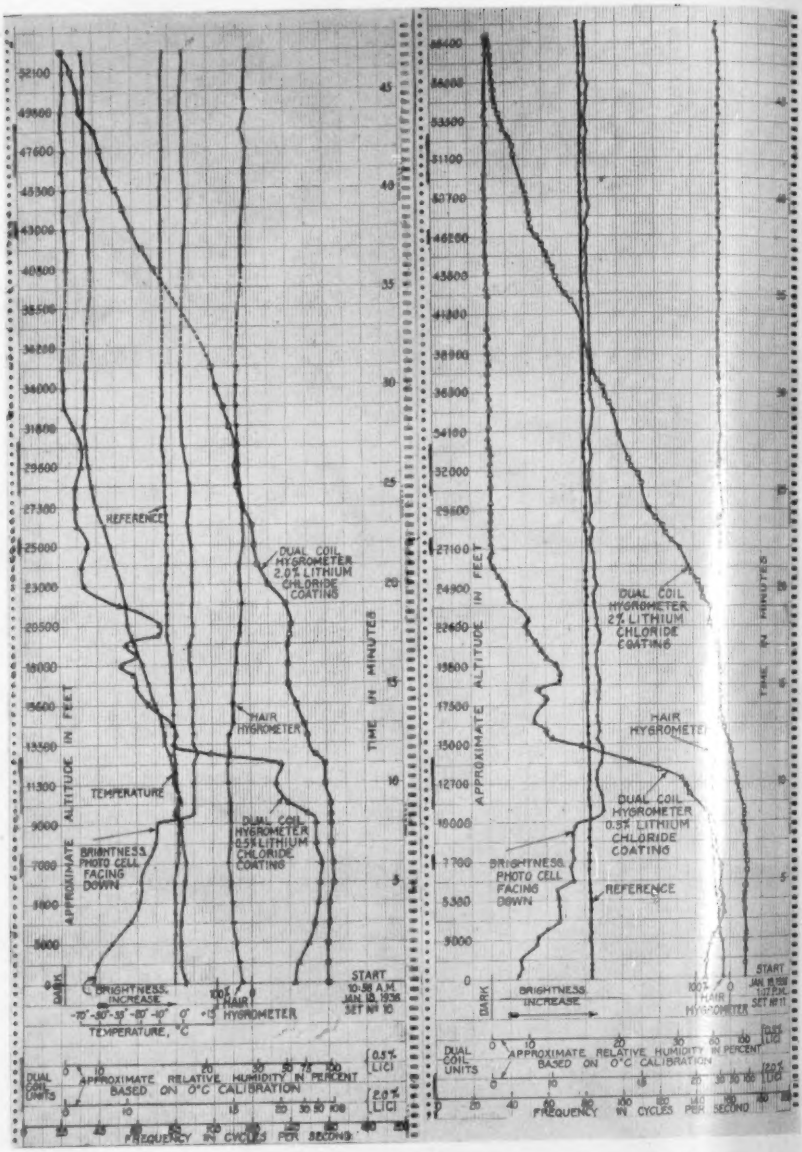

APPROXIMATE ALTITUDE IN FEET
TIME IN MINUTES
REFERENCE
DUAL COIL HYGROMETER 2.0% LITHIUM CHLORIDE COATING
HAIR HYGROMETER
TEMPERATURE
DUAL COIL HYGROMETER 0.5% LITHIUM CHLORIDE COATING
BRIGHTNESS, PHOTO CELL FACING DOWN
DARK
BRIGHTNESS INCREASE
100% HAIR HYGROMETER 0
TEMPERATURE, °C
START 10:58 A.M. JAN. 18, 1938 SET № 10
DUAL COIL UNITS
APPROXIMATE RELATIVE HUMIDITY IN PERCENT BASED ON 0°C CALIBRATION
0.5% LiCl
2.0% LiCl
FREQUENCY IN CYCLES PER SECOND
DUAL COIL HYGROMETER 2% LITHIUM CHLORIDE COATING
START JAN. 18, 1938 12:22 P.M. SET № 11

FIGURE 22.—*Graph at the left plotted from January 18, 1938, flight record as received at a second receiving station.*

Graph at the right plotted from a record of a second flight on January 18, 1938. In each flight the type radio meteorograph shown in figures 14–16 was used.

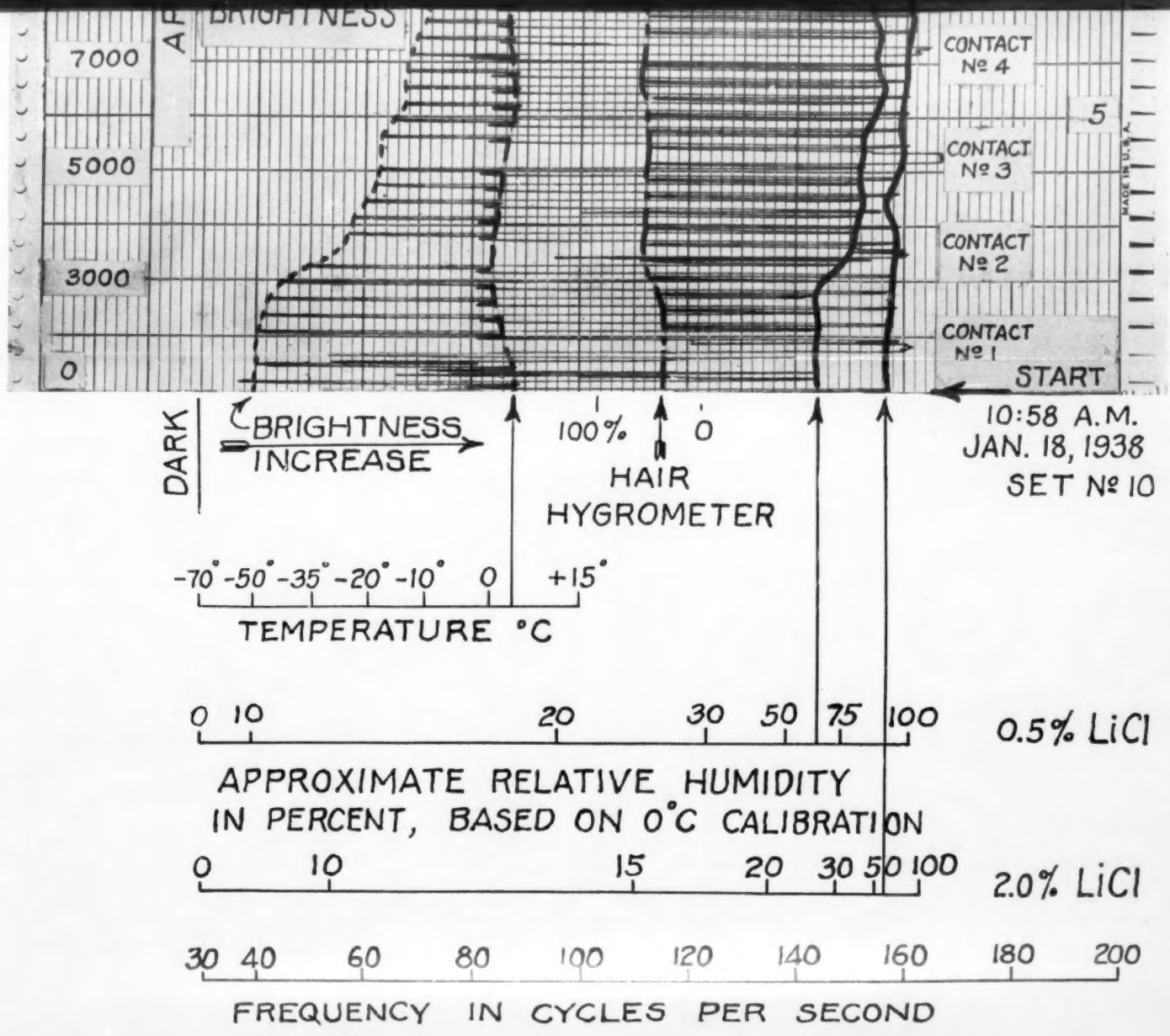
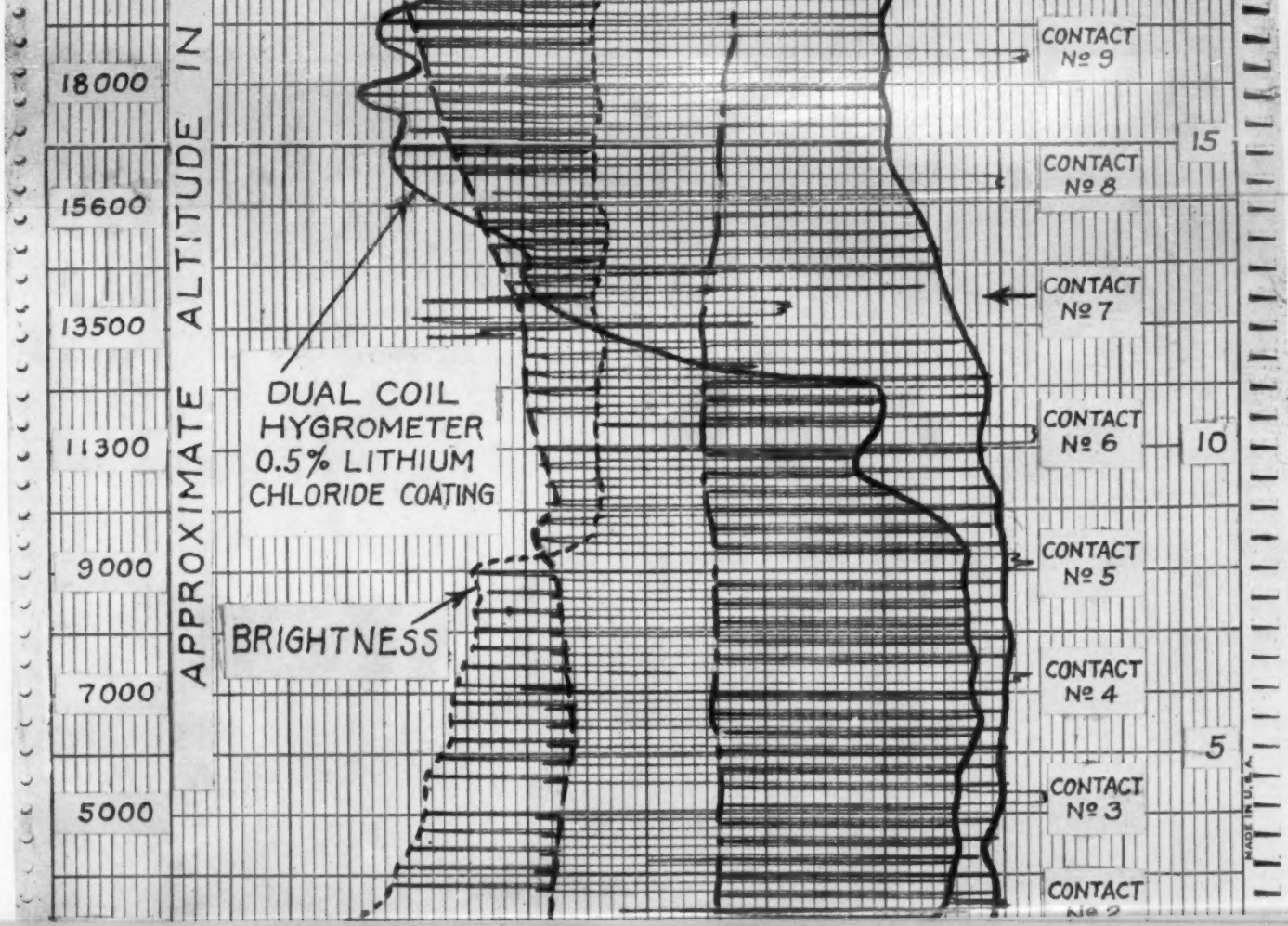
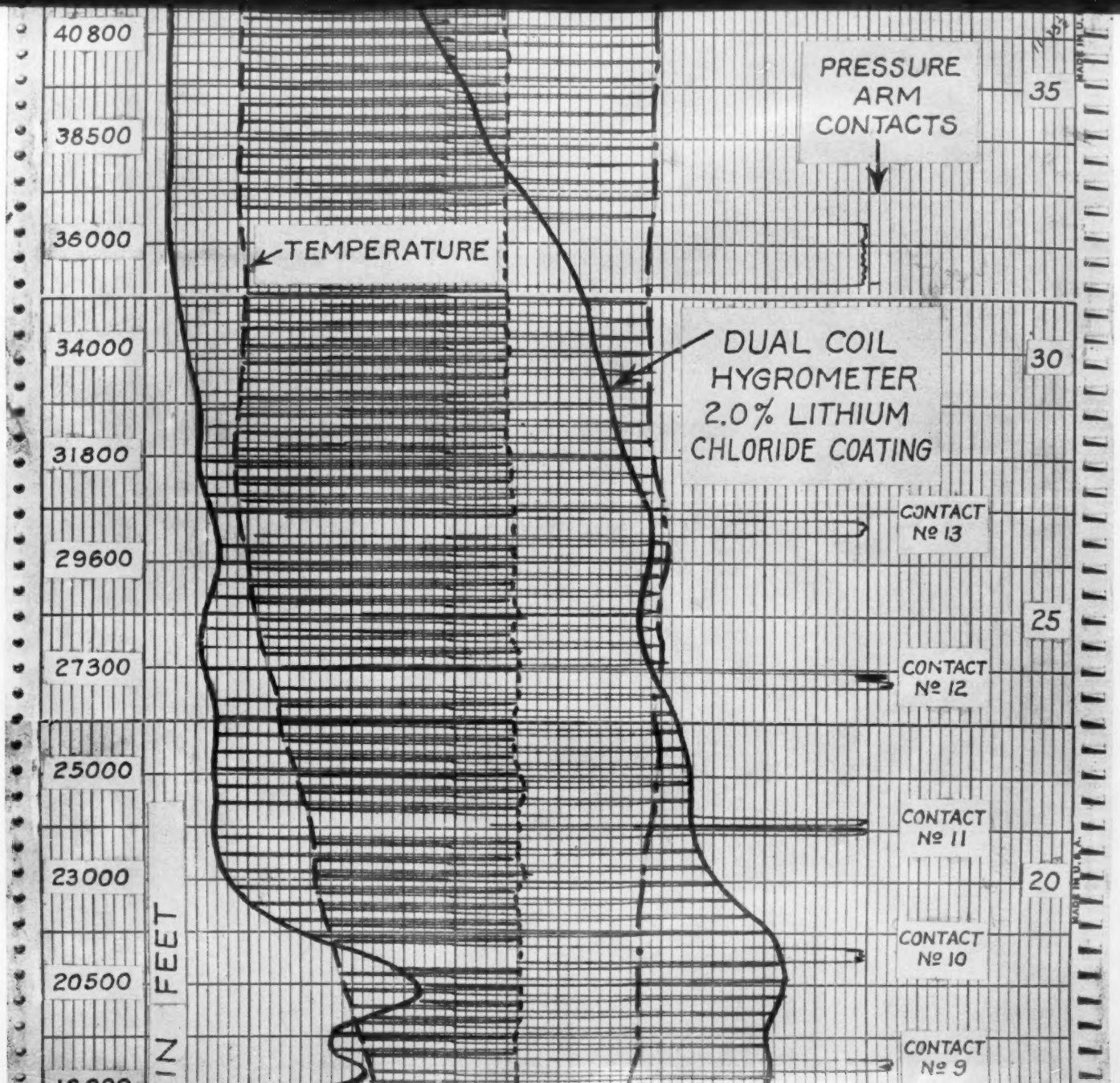
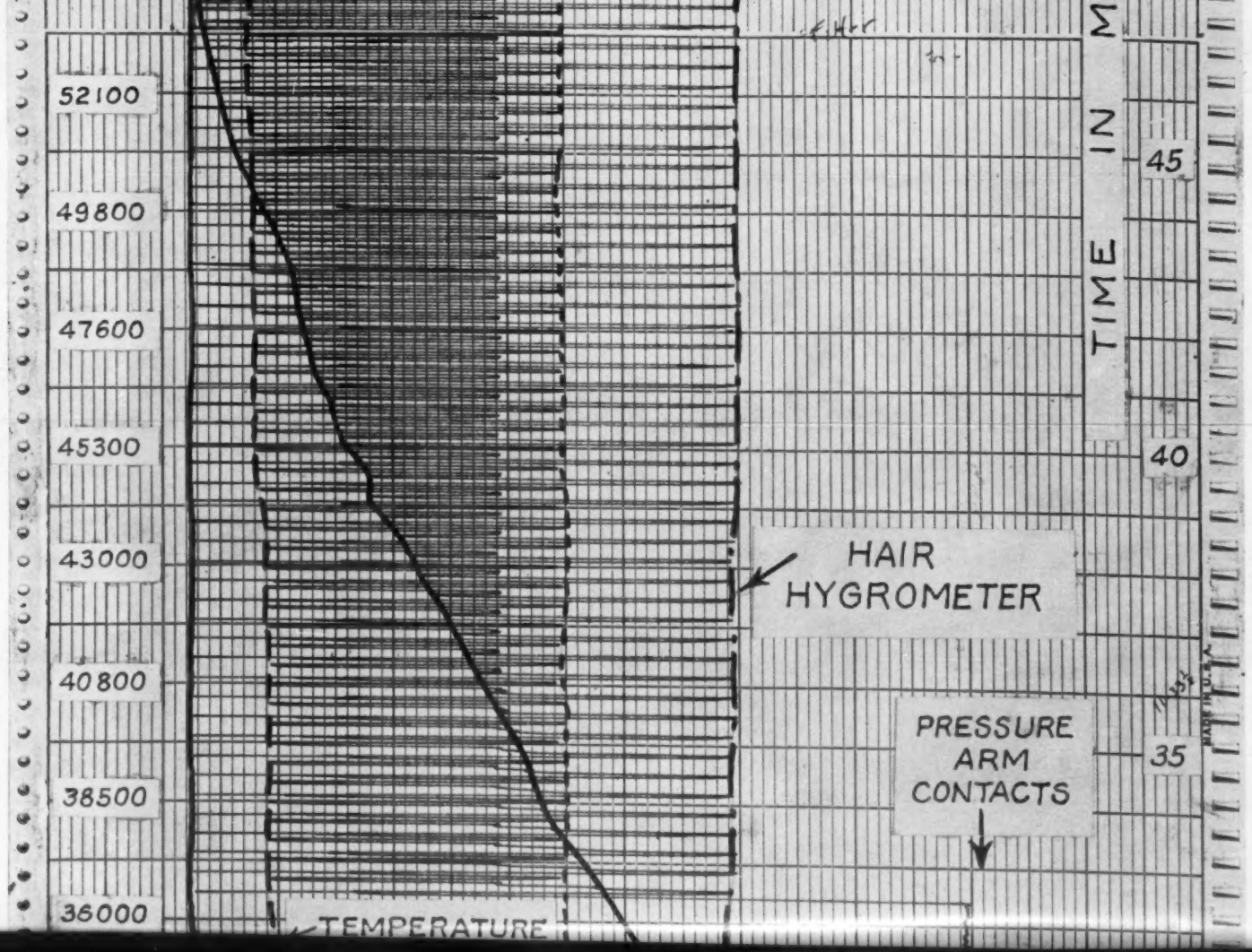


FIGURE 21.—*Flight record obtained on January 18, 1938, using the radio-meteorograph unit shown in figures 14, 15, and 16.*


APPROXIMATE ALTITUDE IN
18000
15600
13500
11300
9000
7000
5000
DUAL COIL
HYGROMETER
0.5% LITHIUM
CHLORIDE COATING
BRIGHTNESS
CONTACT Nº 9
CONTACT Nº 8
CONTACT Nº 7
CONTACT Nº 6
CONTACT Nº 5
CONTACT Nº 4
CONTACT Nº 3
CONTACT Nº 2
15
10
5
MADE IN U.S.A.


40800
38500
36000
34000
31800
29600
27300
25000
23000
20500
IN FEET
PRESSURE ARM CONTACTS
35
TEMPERATURE
DUAL COIL HYGROMETER 2.0% LITHIUM CHLORIDE COATING
30
CONTACT Nº 13
25
CONTACT Nº 12
CONTACT Nº 11
20
CONTACT Nº 10
CONTACT Nº 9


52100
49800
47600
45300
43000
40800
38500
36000
TIME IN MI
45
40
35
HAIR
HYGROMETER
PRESSURE
ARM
CONTACTS
TEMPERATURE

56600

62300

68000

63000

START OF DESCENT

MINUTES

50

55

60

70

MADE IN U.S.A.

MADE IN U.S.A.

63000

58000

53000

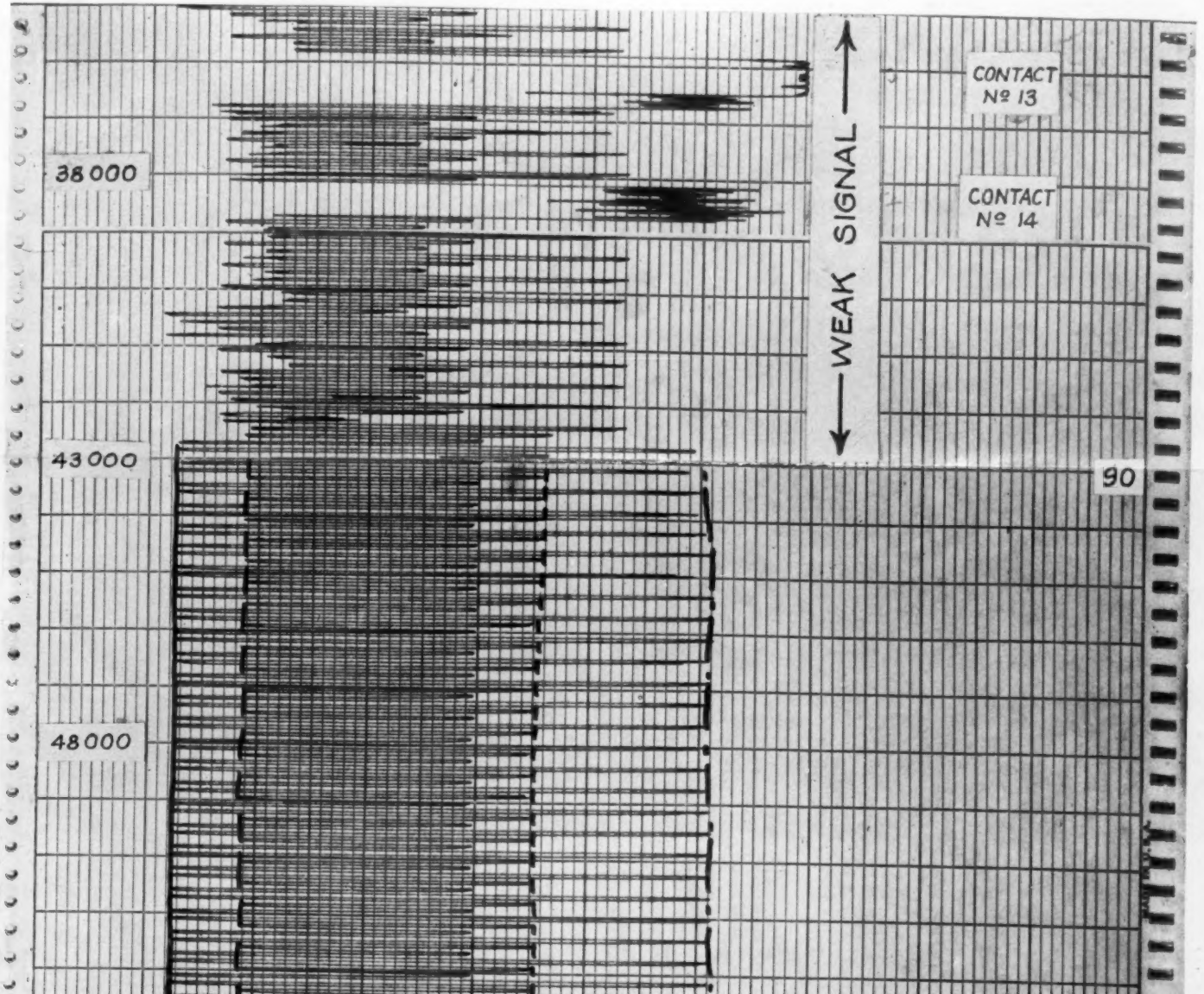
70

80

START OF

MADE IN U.S.A.

UNIV. OF MICH.



below the radio meteorograph. The long dotted-line trace is that for temperature. The dash-dot line is a record of the humidity variations as given by the hair hygrometer. The full lines to the left and right are the humidity traces for the dual-coil hygrometers with 0.5 and 2.0 percent LiCl, respectively. It should be noted that the graph for the hair unit is the reverse from that of the two dual-coil units.

While all the measurements are more or less qualitative because of the difficulty of calibrating the dual-coil units at low temperatures, the results are comparative. Because of lack of calibration of the units, no correction is made in the humidity scale for temperature. Actually, the humidities indicated are higher, in a degree depending upon how much the ambient temperature is below 0° C. Figure 22 at the left shows graphs plotted from a record of the first flight obtained at a second receiving station. It is interesting to note that above an altitude of 35,000 ft (temperature of approximately −60° C) the 0.5 percent LiCl coated hygrometer unit ceased to function, while the 2 percent coated unit continued to show a decrease in humidity up to 55,000 ft where it became too dry for it to register. The major humidity changes above 10,000 ft recorded by the H_1 (0.5-percent coating) unit are also indicated by the H_2 (2-percent coating) unit at approximately the same altitudes. While the scale of humidity indications for the hair hygrometer is contracted in comparison with the electrical hygrometer units, nevertheless, close examination will show that it does not indicate many of the variations shown by the latter.

Major changes, such as those registered by unit H_1 between 12,000 and 13,500 ft, were not shown by the hair until a minute or so later. The temperature was approximately −6° C. This lag, which is equivalent to 1,100 ft, becomes greater at lower temperatures. A humidity drop indicated by both H_1 and H_2 units occurring between 20,500 and 23,000 ft is not indicated by the hair graph until 2 minutes later, occurring between 23,000 and 25,000 ft. The temperature in this instance was approximately −28° C.

A continuous record such as that shown in figure 21 and at the left in figure 22, produced practically simultaneously by three devices measuring temperature, humidity, and brightness, respectively, without appreciable lag in their response, makes possible a more intelligent analysis of the data than is possible where only temperature and humidity measurements are obtained at infrequent intervals. For example, note the correlation of the light variations with temperature and humidity changes, particularly at 9,500 ft, where the brightness graph shows that the balloon was just rising out of the last cloud layer, between 9,000 and 9,500 ft. Both temperature and humidity show sudden changes.

The full flight record shown in figure 21 indicates that the balloon reached an approximate altitude of 70,000 ft. The 14 pressure-contact signals shown to the right in the graph give the rate of ascent up to 35,000 ft. A previous calibration in a pressure chamber gave the approximate height corresponding to each pressure contact. From the rate of ascent the approximate maximum altitude of 70,000 ft was determined. Except for minor temperature variation, the humidity and light graphs show little variation above 55,000 ft. The discontinuities in the graph below 43,000 ft during the descent were caused by low battery voltage due to extreme cold.

The record for the second flight made 2¼ hours after the first one is shown at the right in figure 22. The sky was still overcast. The same general humidity variations are registered in this flight and at approximately the same altitudes as were shown in the first flight record. This record is therefore helpful in that it shows that the dual-coil units may be relied upon to give a true indication of the humidity structure of the atmosphere, even in the present stage of development.

IX. CONCLUSION

The electrical-type hygrometer appears to offer a new tool for the measurement of humidity in the upper atmosphere.

Further flight tests and development of means for calibrating this type of device at low temperatures seem to be all that is now necessary to adapt it to routine measurements in the upper atmosphere.

The author expresses his appreciation to H. Diamond for many helpful suggestions during the progress of this work; to E. G. Lapham and W. S. Hinman, Jr., of the Bureau's radio section, for assistance in the electrical design of the radio meteorograph and the flight tests; to L. L. Hughes, of the radio section, for his skillful construction and contribution to the mechanical design of the radio-meteorograph units used in the flight tests; to C. P. Saylor, E. R. Smith, and E. Wichers, of the Bureau's Chemistry Division, for assistance in choice of coatings for the hygrometer units; to E. O. Sperling, of the glass blowing shop, for ground-glass samples. Special acknowledgment is due to W. G. Brombacher, W. A. Wildhack, and B. W. Woolard, of the aeronautic instrument section, for the temperature-humidity measurements.

WASHINGTON, *March 14, 1938.*

[AUTHOR'S NOTE.—Recent experiments with a dual-coil unit wound with platinum wire showed very little change in resistance of the unit with time. This indicates that the long-period aging is due to a resistance film on the wire where it contacts the glass. A less corrosive wire than tinned copper should therefore be used. It is expected that noncorrosive materials, such as palladium, michrome, nickel, or Alleghany electric metal might be found satisfactory.]

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NEW PROCEDURE FOR THE ANALYSIS OF DENTAL GOLD ALLOYS[1]

By Raleigh Gilchrist

ABSTRACT

From a study of conditions under which certain base metals known to be associated with native grain platinum could be collectively separated from the platinum metals and gold, a new procedure has been developed for analyzing dental gold alloys which differs essentially from that published by W. H. Swanger in 1926.

The procedure as applied to dental gold alloys provides for the separation and gravimetric determination of silver, iridium, tin, gold, indium, copper, zinc, nickel, palladium, rhodium, and platinum. Briefly it is as follows: Silver chloride and metallic iridium are precipitated when the alloy is decomposed by aqua regia. Tin is next separated by a new technic of controlled hydrolysis. Gold is then precipitated by sodium nitrite, and next, by adjusting the alkalinity with sodium hydroxide to the end point of thymolphthalein, indium, copper, zinc, and nickel are collectively separated from rhodium and platinum. At this alkalinity a small proportion of palladium precipitates with the base metals but is recovered from them with dimethylglyoxime. Palladium, rhodium, and platinum are separated from one another by the usual methods of this laboratory. The four base metals are separated, in order, by precipitating indium with ammonium hydroxide, copper, and subsequently zinc, with hydrogen sulfide, and nickel with dimethylglyoxime.

It was found that manganese, iron, cobalt, and chromium are also quantitatively precipitated in a solution containing nitrite at the end point of thymolphthalein, and that it is possible to separate lead from palladium and platinum at the end point of xylenol blue, if the lead is precipitated as carbonate.

Suggestions are made for using the procedure as a refining method for crude material containing gold and the platinum metals.

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 94th Meeting of the American Chemical Society, held in Rochester, N. Y., September 6 to 10, 1937.

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I. INTRODUCTION

Although the primary object of the experiments herein described was the investigation of conditions under which certain base metals known to be associated with native grain platinum could be collectively separated from the platinum metals and gold, the scope of this paper has been restricted to the detailed consideration of those base metals and precious metals which are found in dental gold alloys. Modern dental gold alloys always contain silver, gold, and copper; frequently contain palladium, platinum, tin, and zinc; and occasionally contain iridium, rhodium, nickel, and indium. Indium [2] has been introduced into dental gold alloys recently. In addition, magnesium, aluminum, manganese, and iron have been found in rare instances.

With the exception of indium and zinc, the base metals which have been mentioned, as well as cobalt and chromium, are encountered in the analysis of native grain platinum. Native platinum also contains the two additional platinum metals, osmium and ruthenium.

While the recommended procedure is designed specifically for the analysis of dental gold alloys, it is likewise applicable to native platinum, because, under the conditions specified for the quantitative collective precipitation of indium, copper, zinc, and nickel, the additional metals iron, cobalt, manganese, and chromium are also completely precipitated.

Nearly 12 years have elapsed since Swanger,[3] at the National Bureau of Standards, published the only existing method for the complete analysis of dental gold alloys. Although his method is still reliable, certain analytical improvements in handling some of the constituent elements, and the addition of the rare metal indium to such alloys, make a revision of the analytical scheme desirable. The new procedure differs essentially from that of Swanger, but it necessarily retains certain features of his method. The two procedures are identical up to the point where tin is separated. Swanger's directions are likewise followed for the recovery of palladium and of nickel by dimethylglyoxime and of zinc by hydrogen sulfide. For the determi-

[2] N. O. Taylor, U. S. Patents 1,987,451 and 1,987,452, January 8, 1935.
[3] W. H. Swanger, *Analysis of dental gold alloys*, BS Sci. Pap. **21**, 209 (1926) S532.

nation of aluminum, iron, manganese, and magnesium, Swanger's procedure is also recommended.

The chief feature of the new method is the collective separation of indium, copper, zinc, and nickel from platinum, palladium, and rhodium by precipitation with sodium nitrite and sodium hydroxide at the end point of thymolphthalein. Another essential feature is the precipitation of gold by sodium nitrite.[4] A third is an improved procedure for the hydrolytic precipitation of tin. It is to be noted that the procedure provides for the separation and determination of indium, and also that it is so designed that a preliminary qualitative analysis of the alloy is unnecessary.

1. THE METHOD OF SWANGER

The essential features of Swanger's method are as follows: The alloy is attacked by diluted aqua regia, which leaves silver chloride as an insoluble residue. If iridium is contained in the alloy, it separates in metallic form and is found with the silver chloride. If the alloy contains much platinum and palladium, the silver chloride will also be contaminated by these two metals, and, if the iridium content is over 0.2 to 0.3 percent, the metallic iridium may be contaminated by a significant amount of platinum. If platinum metals occur in the alloy, it is necessary to dissolve the silver chloride deposit in ammonium hydroxide and to reprecipitate it by adding nitric acid. In this operation the iridium is isolated and can be caught and determined. If the iridium contains a significant amount of platinum, it can be refined by fusion with lead.[5] The small amount of platinum and palladium, recovered from the reprecipitation of the silver chloride, is added to the original filtrate from the removal of silver chloride, after suitable treatment to convert these metals again to chloro-acids.

When the alloy contains tin, it is removed at this stage by the action of sodium acetate. It is usually necessary to refine the stannic acid so obtained by a reprecipitation with ammonium acetate from a solution of its sulfate in sulfuric acid.

Before proceeding with the separation of gold, it is necessary to eliminate the acetate which has been added, because of its interference in subsequent analytical operations. Swanger recommended that this be done by heating the evaporated solution with sulfuric acid until fumes of this acid are evolved. It has been the writer's experience that as much as 2 percent of the gold may be lost in this treatment, presumably through volatilization as gold chloride. Ten or more years of experience with Swanger's method have shown that this is the only apparent defect in the procedure, and is encountered only under the circumstances mentioned. The elimination of acetic acid could probably be accomplished at the temperature of the steam bath with no loss of gold.

Gold is precipitated as metal by sulfur dioxide, and must be reprecipitated by oxalic acid if the alloy contains platinum or palladium, since these two metals contaminate the first gold precipitate. Palladium is next separated, after suitable preparation of the filtrates from the gold precipitations, by means of dimethylglyoxime; but it must be reprecipitated to insure freedom from contamination by platinum.

[4] E. Leidié, Compt. rend. **131**, 888 (1900). Leidié, in a note presented to the French Academy of Sciences, suggested a scheme for separating gold and the base metals from the platinum metals in native platinum by means of sodium nitrite and sodium carbonate. His paper, however, contains only general directions of procedure and no experimental data.

[5] R. Gilchrist, J. Am. Chem. Soc. **45**, 2820 (1923); BS Sci. Pap. **19**, 325 (1924) S483.

After destruction of residual dimethylglyoxime, copper is precipitated by ammonium thiocyanate from a solution saturated with sulfur dioxide and having a definite acidity. When palladium is absent, copper can be precipitated directly after removing the gold. Platinum contaminates the normally white cuprous thiocyanate so that again a reprecipitation is necessary, if accurate results are desired.

After the removal of copper, the metals remaining are platinum, rhodium, nickel, zinc, (manganese, and magnesium). Platinum and rhodium are precipitated together by hydrogen sulfide and later separated from each other by the hydrolytic method of Wichers,[6] which consists in precipitating the rhodium by means of a suspension of barium carbonate. Nickel, zinc, and manganese are recovered by conventional methods. In the case of magnesium and of iron, neither of which is often encountered in dental alloys, Swanger recommends starting with a fresh sample and removing interfering elements with hydrogen sulfide, before proceeding with their determination.

II. PROCEDURE RECOMMENDED FOR THE ANALYSIS OF A DENTAL GOLD ALLOY

The new procedure provides for the separation and gravimetric determination of silver, iridium, tin, gold, copper, zinc, nickel, palladium, rhodium, and platinum, as does Swanger's procedure, and of indium as well. The order of the various steps is such that a prior qualitative analysis will usually not be necessary because proving the presence or absence of a particular metal, with the exception of indium, involves no delay or change in the orderly procedure.

The procedure as written is designed to yield results of a high degree of accuracy. Whenever results of a lesser degree of accuracy are satisfactory, it will undoubtedly be possible to save time by omitting certain steps, such as some of the double precipitations. An attempt has been made to indicate the magnitude of some of the errors that may result from such a simplification of the procedure, but judgment and experience in the use of the method will be needed to determine how much can be done in this direction.

1. PREPARATION OF THE SAMPLE

Dental gold alloys are usually received for analysis in the form of wires, bands, or plates. To obtain as uniform a sample as possible and to insure complete disintegration of the alloy by acids, it is desirable to roll the specimen to a ribbon or sheet about 0.003 to 0.005 inch in thickness and to cut the rolled specimen into small pieces about one-sixteenth to one-eighth of an inch square. A sample weighing 2 g, composed of the small pieces taken at random, is recommended.

2. THE PROCEDURE

Place 2 g of the prepared sample in a covered 250-ml beaker, add 25 ml of diluted aqua regia,[7] and set on the steam bath. With the exception of silver, which separates as the insoluble chloride, and of

[6] E. Wichers, J. Am. Chem. Soc. 46, 1818 (1924).

[7] Throughout this paper, whenever acids are mentioned, hydrochloric acid will mean the concentrated acid of specific gravity 1.18; nitric acid, the concentrated acid of specific gravity 1.42; and sulfuric acid, the concentrated acid of specific gravity 1.84.

Diluted acids will be designated as follows: For example, diluted hydrochloric acid (1+99) will mean 1 volume of the concentrated acid of specific gravity 1.18 diluted with 99 volumes of water.

Diluted aqua regia will mean 4 volumes of hydrochloric acid of specific gravity 1.18 and 1 volume of nitric acid of specific gravity 1.42, diluted with 6 volumes of water.

Ammonium hydroxide will mean the solution of specific gravity 0.90.

iridium, which separates as metal, all the constituents of the alloy will pass into solution.[8] It is advisable to break up the silver chloride, which usually retains the shape of the original metallic pieces, with a glass rod from time to time, to insure complete disintegration. If the solution contains tin, care must be taken that it does not evaporate to dryness.

When decomposition of the alloy is complete, dilute the solution to a volume of 150 to 200 ml, allow it to stand on the steam bath for about 1 hour, and then set it aside to cool.

(a) DETERMINATION OF SILVER

(1) *In the Absence of Platinum Metals.*—If the alloy is known not to contain platinum metals, either by preliminary qualitative analysis or otherwise, collect the silver chloride by filtering through a porcelain filtering crucible,[9] using suction. Wash the precipitate well with water, dry it at 110° C, weigh it, and calculate its silver content, using the theoretical factor 0.7527.

(2) *In the Presence of Platinum Metals.*—Of the platinum metals only iridium separates quantitatively with the silver chloride, but enough palladium and platinum are also retained to discolor the silver chloride and to necessitate its reprecipitation if an accurate determination of silver is wanted, even if iridium is absent.

If the alloy contains platinum metals, catch the silver chloride on a 9-cm filter of close texture [10] and wash it well with water. Reserve the filtrate.

Dissolve the precipitate of silver chloride with two 25-ml portions of hot diluted ammonium hydroxide (1+1). Wash the beaker, rod, and cover, as well as the filter, with hot diluted ammonium hydroxide (1+99), from a wash bottle. This treatment is probably sufficient to effect the complete removal of silver chloride, but it is advisable to digest the filter itself with an additional 25-ml portion of the diluted ammonium hydroxide, which is then filtered to remove paper pulp, and to recover iridium if present. After a final washing of the filter and paper pulp with hot diluted ammonium hydroxide (1+99), the total volume of the filtrate and washings will be about 200 ml.

Acidify the ammoniacal solution with nitric acid to reprecipitate the silver as chloride, allow it to stand until the supernatant liquid is clear (usually overnight), filter through a porcelain filtering crucible, and finish the determination as previously directed.

If the silver chloride has been dissolved in ammonium hydroxide and reprecipitated, because it was contaminated by platinum and

[8] Small amounts of rhodium enter into dental gold alloys through the use of impure platinum or palladium. Such amounts, usually only a small fraction of 1 percent, are completely dissolved when the alloy is attacked with diluted aqua regia. There appears to be a limit, however, to the amount of rhodium which can be alloyed with gold and subsequently dissolved when the alloy is treated with acids.

If rhodium is added intentionally to the alloy, even within the limit of subsequent complete solubility, sufficient time of melting may not have been allowed for thorough alloying, and, as a result, some rhodium will be found with the deposit of silver chloride.

In the case of iridium there appears to be no limiting range within which this metal will subsequently be dissolved when the dental gold alloy is attacked. The entire amount of iridium will be found with the deposit of silver chloride.

[9] This type of crucible is manufactured by the State Porcelain Works, Berlin, Germany, and is now available in the United States. A crucible of convenient size is one having a height of 40 mm, a diameter at the top of 35 mm, a diameter at the bottom of 23 mm, a capacity of 25 ml, and a porosity designated by the number "2."

A crucible of this kind is much more convenient to use than the customary Gooch crucible with an asbestos pad. This crucible is likewise excellent for catching the glyoxime precipitates of nickel and palladium. It is especially recommended in the filtration of the hydrolytic precipitates of palladium, rhodium, and iridium, in their separation from platinum, since it avoids the introduction of organic matter, which causes interference in subsequent reprecipitation. No doubt, glass crucibles of suitable porosity could be used.

[10] In the experiments reported in this paper, S. & S. No. 589 blue ribbon filters were used. When solutions were filtered to remove paper pulp or traces of silica, a thinner filter, S. & S. No. 590, was used.

palladium, a filtrate will be obtained which contains the traces of these two metals in the form of ammine-compounds. Although this filtrate will contain no tin, it is as convenient at this stage as later to recover the small amounts of platinum and palladium in suitable form and to unite them with the main solution of the alloy. In order to convert the ammine-compounds of these two metals to their chloro-acids, evaporate the filtrate from the second precipitation of silver chloride, destroy the ammonium nitrate which it contains by treatment with hydrochloric and nitric acids, add 5 ml of sulfuric acid, and heat until fumes of sulfuric acid are evolved. Add a few milliliters of nitric acid and then heat the solution until practically all the sulfuric acid is eliminated. Add a few milliliters of diluted aqua regia to dissolve any metallic deposit, and then add, without filtering, the residual solution to the filtrate and washings from the original silver chloride precipitation. The volume of the combined solutions at this stage will be about 300 ml. Reserve for the determination of tin.

(b) DETERMINATION OF IRIDIUM

Ignite in a porcelain crucible the paper and residue obtained from the extraction of the silver chloride with ammonium hydroxide. Ignite the resulting residue in hydrogen, cool it in hydrogen, and weigh it as metallic iridium.

According to Swanger, if the iridium content is greater than about 0.3 percent, the iridium residue may contain a trace of platinum. If the iridium content of the alloy is substantial, and an accurate determination of it is desired, the two metals can be separated from each other by fusion with lead.[11]

(c) DETERMINATION OF TIN

Heat the solution, which was reserved for the determination of tin, to boiling and neutralize it with a freshly prepared solution of sodium hydroxide until its acidity is decreased to about pH 1.5, as ascertained by means of the indicator thymol blue,[12] which changes color from red to orange. Boil the solution for 5 minutes and then set it on the steam bath for 15 to 20 minutes. If no precipitate is obtained, proceed with the precipitation of gold by sodium nitrite.

If a precipitate of stannic acid is obtained, catch it on a 9-cm filter of close texture, which contains some paper pulp. Wash the filter and precipitate thoroughly with hot water which is acidified with sulfuric acid between the limits of pH 4 (end point of bromphenol blue) and pH 1.5. Return the filter with its contents to the beaker in which the precipitation was made, add 5 ml of sulfuric acid, and destroy organic matter by repeatedly adding nitric acid and subsequently heating to the fuming point of the sulfuric acid. A small amount of

[11] R. Gilchrist, J. Am. Chem. Soc., **45** 2820 (1923); BS Sci. Pap. **19**, 325 (1924) S483.

[12] Thymol blue, which is thymolsulfonphthalein, undergoes two color changes: one, a change from red to orange, which is utilized here in the precipitation of tin; the other, a change from yellow to blue, which is utilized later in the procedure in the collective precipitation of indium, copper, zinc, and nickel.

Since the solutions being neutralized are usually highly colored or contain precipitates, the method which is used throughout the procedure for determining the end point is to allow a drop of a 0.01-percent solution of the indicator to react with a drop of the solution on the end of a stirring rod. This method is not that of the usual "outside indicator." The operation is performed by lifting the stirring rod above the level of the solution and testing the drop which clings to it. The stirring rod is then replaced in the solution with no loss of material. The end point determined in this way is practically identical with that determined by adding the indicator directly to the main body of the solution. The sulfonphthalein indicators enumerated in this paper were prepared by forming their monosodium salts and then diluting to a concentration of 0.01 percent.

gold which invariably contaminates the first precipitate of stannic acid will separate as metal during the fuming operation. If, however, a purplish cloud appears when the solution is diluted in the next operation, the trace of gold has not been properly coagulated, and the solution must be digested again at the fuming point of the sulfuric acid.

Dilute the concentrated acid solution to 50 ml, and, because of the instability of stannic sulfate, keep it cool and filter it immediately through a 7-cm thin paper of close texture. Wash the filter thoroughly with diluted sulfuric acid (1+99), at room temperature. The recovered gold is treated as is described in the section of the procedure dealing with the collective precipitation of gold, indium, copper, zinc, and nickel.

Dilute the solution of stannic sulfate to a final volume of 200 ml and set it on the steam bath for 1 hour, at a temperature of about 85° C. Catch [13] and wash the resulting precipitate as previously directed. It is to be noted that the precipitate of stannic acid obtained under these conditions differs in character from that obtained during the first precipitation, and that it has a tendency to form a slight film on the glass, which is not always readily removable. This may cause an error of about 0.5 mg in the determination of the tin. It is therefore recommended that clean, unetched glassware be used for the precipitation, and, if a film is formed which can not be removed by wiping, that it be dissolved in 5 ml of sulfuric acid in the manner previously described. From this solution it is recommended that the small amount of tin then be precipitated by adding 15 g of ammonium acetate, which produces stannic acid similar in character to that obtained when tin is precipitated from its chlorostannate compound at pH 1.5. The filtrate obtained in this acetate hydrolysis is thereafter rejected.

It was found experimentally that the two precipitations specified, namely, the one at pH 1.5 and the other by diluting the solution of stannic sulfate, sufficed to free tin from contamination by other metals under the conditions which obtain in the analysis of these alloys.

Ignite the precipitate of stannic acid carefully in a porcelain crucible until carbonaceous matter is eliminated, and finally ignite the residue at a temperature between 1,100 and 1,200° C, taking care that the flame of the burner does not envelop the crucible. Weigh the residue, which should be white when cold, as stannic oxide, SnO_2. Calculate its tin content, using the theoretical factor 0.7877.

(d) COLLECTIVE PRECIPITATION OF GOLD, INDIUM, COPPER, ZINC, AND NICKEL

The next operation in the scheme of analysis is to precipitate the gold as metal by the reducing action of sodium nitrite, and then, without removing the gold, to precipitate the base metals indium, copper, zinc, and nickel.

In order to unite with the main solution of the alloy the small amount of gold and other metals which contaminated the stannic acid in its first precipitation, add the paper which was used to filter the stannic sulfate solution, and which contains the small amount of recovered gold, to the evaporated filtrate from the second precipitation

[13] Here and elsewhere throughout the procedure, except in the case of silver chloride or when palladium or nickel is to be determined as its glyoxime compound, whenever a precipitate is quantitatively transferred to a filter, it is recommended that the beaker be wiped with a small piece of ashless filter paper to insure complete removal.

of the tin. Destroy organic matter in the customary manner by repeated addition of portions of nitric acid, and then eliminate practically all the sulfuric acid contained in it by heating. Digest the residue with a few ml of diluted aqua regia, filter the solution, and add it to the filtrate obtained from the first precipitation of the tin.

Concentrate the combined solutions to a volume of about 150 ml, and neutralize with sodium hydroxide to the red-orange end point of thymol blue (about pH 1.5).[14] Heat the solution to boiling and add to it 10 ml of a filtered 10-percent solution of sodium nitrite. Boil the solution for 2 or 3 minutes to coagulate the precipitated gold but take care that the solution does not bump. Neutralize the solution with sodium hydroxide until its acidity again corresponds to the red-orange end point of thymol blue.

Add 20 ml of the nitrite reagent and then neutralize the hot, constantly stirred solution by adding dropwise a diluted solution of sodium hydroxide until the alkalinity reaches that which corresponds to a faint blue color of thymol blue. Boil the solution for 5 minutes, again taking care that the solution does not bump. On boiling, the alkalinity of the solution will tend to decrease and must be restored to the end point of the indicator. Under the conditions just described, gold, and the base metals, indium, copper, zinc, and nickel, will be quantitatively precipitated. The precipitate formed by copper will have changed color from bluish white to brown, and the collective precipitate will have shrunk considerably in volume.

When the solution, after precipitation of gold, is neutralized with sodium hydroxide, its color changes from green, caused by copper, to colorless or pale yellow, depending upon the absence or presence of platinum metals, and, at the same time, the base metals precipitate as hydroxides. Platinum metals in the solution are rapidly converted by the nitrite from chloro-acids to complex nitrites which are soluble and stable at an alkalinity corresponding to the end point of cresol red or of xylenol blue (about pH 8), at which alkalinity the precipitate of base metals suddenly coagulates and settles well. The complex nitrites are also stable at an alkalinity corresponding to the change of color from yellow to blue of thymol blue, with the exception of that of palladium, which begins to decompose. It is simpler not to remove the precipitate of metallic gold until after the base metals have been quantitatively precipitated. In this way the quantity of alkali salts which accumulate is kept at a minimum.

Allow the precipitate to settle for 15 to 20 minutes, and, before filtering the solution through an 11-cm paper of close texture, wash the filter with a 1-percent solution of sodium nitrite neutral to the blue end point of thymol blue. Transfer the base metal precipitate to the filter, but preferably allow the bulk of the gold to remain in the beaker. Wash the beaker, the gold precipitate, and the precipitate on the filter with about 100 ml of the same wash solution. Use the wash solution at room temperature. Reserve the nitrite filtrate and washings, which contain the platinum metals.

[14] At the acidity designated the solution will be clear. If the solution is neutralized further, before the addition of sodium nitrite, platinum metals are liable to precipitate as hydroxides. In order to insure complete conversion of the chloro-acids of the platinum metals to soluble complex nitrites, it is recommended that sodium nitrite be added at the acidity corresponding to this end point of thymol blue. At acidities greater than this, the nitrite reagent is rapidly decomposed.

(e) DETERMINATION OF GOLD

Although gold is quantitatively precipitated under the conditions just specified, it was found experimentally, in using the method described to dissolve the base metal precipitate, that a small quantity of it appeared on the filter after the base metals had been collectively precipitated a second time and again dissolved. Unless the small amount of gold is recovered, the determination of gold may be low by as much as 1.5 mg, but usually by not more than 0.5 mg.

Wash the gold deposit and the filter containing the base metal precipitate thoroughly with hot water, to remove residual nitrite solution. If residual nitrite is not removed, it reacts with the hot acid in the subsequent operation and causes the gold to dissolve partially. Dissolve the base metal precipitate off the filter with hot diluted hydrochloric acid. For this purpose, use alternately diluted hydrochloric acid (1+99) and acid of greater strength, such as (1+10) or (1+5). Transfer the gold precipitate from its beaker, rinse this beaker with diluted hydrochloric acid to remove any adhering base metal precipitate, and wash the filter, which now contains the gold, first with hot diluted acid and finally with hot water. Place the filter with its contents in a porcelain crucible.

To insure freedom from traces of platinum and rhodium, as well as to recover a small quantity of gold, the base metals, indium, copper, zinc, and nickel, should be collectively precipitated a second time. It is to be noted that palladium will not be completely eliminated at the alkalinity specified because its complex nitrite begins to decompose. That amount of palladium which persists in contaminating the base metal precipitate is subsequently removed by means of dimethylglyoxime. To make the second precipitation, evaporate to a moist residue the solution obtained when the base metal precipitate was dissolved in hydrochloric acid.

Dissolve the residue in 150 ml of water and make sure that the acidity of the resulting solution does not exceed pH 1.5. Heat the solution to boiling, add 20 ml of the nitrite reagent, and proceed with the precipitation of the base metals as previously described. Wash and redissolve the base metal precipitate as previously directed. If a trace of gold accompanied the solution of the first base metal precipitate, it will appear at this stage as a dark stain on the filter.

Combine this filter with that previously obtained, which contains the bulk of the gold, ignite them at about 900° C, and weigh the residue as metallic gold.

Combine the nitrite filtrate with that obtained in the first precipitation and reserve the solution for the separation of the platinum metals from one another.

(f) RECOVERY OF PALLADIUM FROM THE BASE METALS

Before proceeding with the isolation of indium, it is necessary to remove a small but significant amount of palladium from the solution containing the base metals. To do this, first eliminate the excess of acid from the solution containing indium, copper, zinc, and nickel by evaporating to a moist residue; then add 5 ml of hydrochloric acid and dilute to a volume of 200 ml. Precipitate the palladium at room temperature by adding 10 ml of a 1-percent alcoholic solution of di-

methylglyoxime. Allow the solution to stand for at least 1 hour and then filter it through a small filter of close texture. Wash the filter and precipitate first with diluted hydrochloric acid (1+99) and then with water, the temperatures of which should not exceed that of the steam bath (about 85° C).

Reserve the filter and palladium precipitate until the main portion of palladium is recovered from the nitrite filtrates.

(g) DETERMINATION OF INDIUM

Evaporate to a moist residue the solution containing indium, copper, zinc, and nickel, from which a small amount of palladium has been removed by dimethylglyoxime. Destroy residual glyoxime reagent by repeated addition of nitric acid and subsequent evaporation, so that no nickel will precipitate when the solution is later made ammoniacal. Finally, evaporate the solution twice with hydrochloric acid, add about 1 g of ammonium chloride, and dilute to 200 ml.

Warm the solution, and add ammonium hydroxide until all the copper hydroxide which precipitates redissolves. Digest the solution, filter it through a 9-cm paper, and wash the filter and precipitate with a hot 1-percent solution of ammonium chloride, which is faintly ammoniacal. Remove and reserve the filtrate and washings.

Dissolve the precipitate of indium hydroxide from the filter by washing it with hot diluted hydrochloric acid. It is best to use first diluted hydrochloric acid (1+10), and then to wash thoroughly with diluted acid of the concentration of (1+99). Dilute the solution of indium chloride to 200 ml and repeat the precipitation of indium hydroxide, to eliminate copper, zinc, and nickel completely. Combine the filtrate obtained with that previously reserved, which contains copper, zinc, and nickel.

It is to be noted that obtaining a precipitate with ammonium hydroxide does not prove the presence of indium, because aluminum and iron precipitate under the same conditions. The identity of indium is established by its subsequent precipitation as a yellow sulfide, under conditions which prevent the precipitation of aluminum and iron.

Again dissolve with hot acid, as before, the precipitate obtained by the second treatment with ammonium hydroxide, add 5 ml of sulfuric acid, evaporate on the steam bath, add a few millimeters of nitric acid, and then heat the solution until fumes of sulfuric acid are evolved. Dilute the resulting solution of indium sulfate to 50 ml, neutralize it with ammonium hydroxide to the end point of methyl red, added directly to the solution, and then add 2 ml of diluted sulfuric acid (1+17). Dilute the solution to a final volume of 150 ml. The desired acidity to be established for the precipitation is approximately 0.02 *N*.

Pass hydrogen sulfide into the solution at room temperature for 1 hour. Allow the solution to stand until the precipitate settles, then filter it through a 9-cm paper of close texture and wash with water containing 1 ml of diluted sulfuric acid (1+17) in a volume of 150 ml (0.01 *N*), at room temperature. Ignite the filter and precipitate carefully at first and finally at a temperature not above 1,000° C. Weigh the residue as indic oxide, In_2O_3, and calculate its metallic content, using the theoretical factor 0.8270.

(h) DETERMINATION OF COPPER

If the alloy contains no indium, add 10 ml of sulfuric acid [15] to the solution containing the copper, zinc, and nickel, and residual glyoxime if palladium had to be removed. Heat the solution until fumes of sulfuric acid are evolved, and destroy organic matter by means of nitric acid, in the usual way.

If the alloy contained indium, concentrate by evaporation to about 50 ml the combined filtrates and washings from the precipitation of indium as hydroxide. Cautiously add nitric acid to the covered beaker to destroy the accumulated mass of ammonium chloride, and then evaporate to dryness. Dissolve the residue in 20 ml of water, add 10 ml of sulfuric acid, and heat the solution until fumes of sulfuric acid are evolved.

In either instance dilute the solution to 100 ml and filter it to remove traces of silica.

Dilute the solution to a final volume of 400 ml, heat it to the temperature of the steam bath (about 85° C), and precipitate the copper by passing in a stream of hydrogen sulfide for 30 minutes. Filter the solution immediately through an 11-cm paper of close texture and wash the filter and precipitate thoroughly, at room temperature, with diluted sulfuric acid (1+300) which is saturated with hydrogen sulfide.

Dry the filter and precipitate and ignite them carefully in a porcelain crucible. Too rapid ignition causes the sulfide to melt, with danger of mechanical loss by spattering. If, however, the initial heating is done very slowly, the sulfide is converted to oxide without melting. Wipe down the walls of the crucible with a piece of moistened ashless filter paper, and then ignite the residue in air and finally in hydrogen. Cool the reduced metal in hydrogen and weigh it as metallic copper.[16]

(i) DETERMINATION OF ZINC

Evaporate the filtrate and washings from the precipitation of copper as sulfide, add a few milliliters of nitric acid, and heat until fumes of sulfuric acid are copiously evolved. Dilute the solution to 50 ml, neutralize the acid in it with ammonium hydroxide to the end point of methyl red, as was done in the case of indium, add 1 ml of diluted sulfuric acid (1+17), and dilute to a final volume of 150 ml. The desired acidity to be established for the precipitation is 0.01 *N*. Precipitate the zinc by passing hydrogen sulfide into the solution for 1 hour, at room temperature.

Allow the solution to stand for about 2 hours and then filter it through a 9-cm paper of close texture, which contains some paper pulp. Wash the filter and white precipitate of zinc sulfide with a filtered 1-percent solution of ammonium sulfate, at room temperature. Dry the filter and precipitate and ignite them carefully in a porcelain crucible. Burn out carbonaceous matter at as low a tem-

[15] 5 ml of sulfuric acid is sufficient to cover the bottom of a 600-ml beaker, if the bottom of the beaker is flat. Often, however, the bottom of the beaker is not flat and its center becomes dry during the fuming operation. Furthermore, if the accumulated mass of ammonium salts resulting from the removal of indium has not been completely decomposed, the solution may not contain enough sulfuric acid to produce fumes of this acid on heating. Since additional acid has no deleterious effect on the subsequent recovery of zinc and of nickel, and since it is desired to effect a clean separation of copper from zinc in one operation, 10 ml of sulfuric acid is recommended, with precipitation from a volume of 400 ml.

[16] For a discussion of the advantages of this method of determining copper over that in which copper is electrodeposited, see p. 767.

perature as possible, and finally ignite at a temperature between 950 and 1,000° C. Weigh the residue as zinc oxide, ZnO, and calculate its metallic content, using the theoretical factor 0.8034.

(j) DETERMINATION OF NICKEL

Digest on the steam bath the solution containing the filtrate and washings from the removal of zinc sulfide to eliminate most of the hydrogen sulfide. Destroy residual hydrogen sulfide by adding bromine water. Add 5 ml of a filtered 10-percent solution of tartaric acid,[17] and then make the solution slightly ammoniacal.

Precipitate the nickel by adding a 1-percent solution of dimethylglyoxime in 95-percent ethyl alcohol. Approximately 4 g of the solid reagent is required to precipitate 1 g of nickel. To provide an excess of the reagent and to insure complete precipitation, use 5 ml of the alcoholic solution for each 10 mg of nickel. Digest the solution on the steam bath for 10 to 15 minutes, make certain that the odor of ammonium hydroxide in it can be detected, and filter through a filtering crucible of either porcelain or glass. Wash the precipitate well with warm water. Test the filtrate, before discarding it, for complete precipitation of nickel, by adding more ammonium hydroxide and dimethylglyoxime.

Dry the glyoxime precipitate at 110° C for 1 hour, and weigh it. Calculate its nickel content, using the theoretical factor 0.2032.

(k) SEPARATION OF PALLADIUM, RHODIUM, AND PLATINUM FROM ONE ANOTHER[18]

The nitrite filtrates, obtained in the collective precipitation of gold, indium, copper, zinc, and nickel, will contain all the platinum and rhodium, and also that portion of the palladium which did not precipitate with the base metals. The procedure for the separation of these metals from one another and for their recovery will depend upon which ones are absent. If rhodium is absent, it may be more convenient to separate palladium from platinum by precipitation with dimethylglyoxime and to repeat the glyoxime precipitation once. If either palladium or platinum alone is to be recovered, the procedure becomes further simplified.

(1) *When the Alloy Contains Palladium, Rhodium, and Platinum.*— If the nitrite solution contains the three metals, palladium, rhodium, and platinum, decompose the residual nitrite in it with hydrochloric acid in a covered beaker, and evaporate it to dryness. Platinum will impart a yellow color to the residue of salt; palladium, a reddish brown color. These colors will mask the pale rose color of small amounts of rhodium. Treat the residue with hydrochloric acid, and again evaporate to dryness. Repeat this treatment several times, in order to decompose nitroso-compounds which may interfere with the hydrolytic precipitation of palladium and rhodium, and proceed with the separation of these two metals from platinum.

To do this, add 2 ml of hydrochloric acid, dilute the solution to 300 ml, heat it to boiling, add 20 ml of a filtered 10-percent solution of sodium bromate, and then neutralize the hot solution with sodium hydroxide to the end point of bromcresol purple (about pH 6). Add 10 ml more of the bromate reagent, boil for 5 minutes, and further neutralize the solution, this time to the end point of either cresol red

[17] Tartaric acid is added to prevent the precipitation of the small quantities of iron which the solution may contain if the separation of indium by ammonium hydroxide has not been made.

[18] R. Gilchrist and E. Wichers, J. Am. Chem. Soc. 57, 2565 (1935).

or of xylenol blue (about pH 8). Add a third 10-ml portion of the bromate reagent and boil for 15 minutes. Under these conditions palladium and rhodium are collectively precipitated as hydrated dioxides, slightly contaminated with platinum.

Filter the solution by suction, using a porcelain filtering crucible. While this method of filtering is recommended, filter paper may be used, since iridium is absent. If the filtering crucible is used, pour the supernatant liquid through first, then transfer the precipitate. Rinse the beaker and wash the precipitate with a hot 1-percent solution of sodium chloride, neutral to cresol red or to xylenol blue. Place the crucible with the precipitate, and also the glass stirring rod, in the beaker used for the precipitation. It may be necessary to remove a small amount of the precipitate which has crept over the lip of the beaker during filtration. This is conveniently done with moistened crystals of sodium chloride on the finger. Replace the watch glass and add 10 ml of hydrochloric acid, pouring most of it into the crucible. Place the covered beaker on the steam bath. Lift the crucible with the stirring rod, wash it with water, and place it in a 250-ml beaker. Leach the porous bottom of the crucible with two 5-ml portions of hydrochloric acid. Combine the leachings with the main portion of the dissolved precipitate, add 2 g of sodium chloride, and evaporate to dryness. Add 2 ml of hydrochloric acid, dilute the solution to 300 ml, and repeat the precipitation of the hydrated dioxides of palladium and rhodium, to insure complete elimination of platinum. Redissolve the precipitate as previously directed.

The separation of palladium from rhodium is accomplished by a single precipitation with dimethylglyoxime. The procedures for the recovery of these three platinum metals are given in the respective sections dealing with their determination.

(2) *When the Alloy Contains Only Palladium and Platinum.*—If the nitrite solution contains only palladium and platinum, decompose the residual nitrite in it as previously directed. Add 10 to 15 ml of hydrochloric acid, dilute the solution to 400 ml, and, after the sodium salts are dissolved, cool the solution to room temperature.

Precipitate the palladium by adding a 1-percent solution of dimethylglyoxime in 95-percent ethyl alcohol. Approximately 2.3 g of the solid reagent is required to precipitate 1 g of palladium. To provide an excess of the reagent and to insure complete precipitation, use 25 ml of the alcoholic solution for each 100 mg of palladium. Allow the solution to stand at room temperature for at least 1 hour and then filter it on an 11-cm paper of close texture. Wash the precipitate and filter with warm diluted hydrochloric acid (1+99). Test the filtrate with additional glyoxime to make certain that a sufficient amount of reagent had been added.

Return the filter with its yellow glyoxime precipitate to the beaker in which the precipitation was made, or, preferably, place it in a 500-ml Erlenmeyer flask which is closed by a short-stemmed funnel. Add 10 ml of sulphuric acid and destroy organic matter by repeated additions of nitric acid, in the usual way. Finally, heat the solution until fumes of sulfuric acid are evolved.

Cool the concentrated acid solution, dilute it with 10 ml of water, and add 5 ml of diluted aqua regia. Warm the resulting mixture to dissolve any platinum which may have separated during the fuming operation, then dilute it to 100 ml and digest it on the steam bath to

effect complete solution of any anhydrous palladium salt. Filter the solution through a thin paper of close texture, to remove silica, and wash the filter with hot diluted hydrochloric acid (1+99). Dilute the solution to a final volume of 400 ml and repeat the precipitation of palladium with dimethylglyoxime, as previously directed.

The manner in which the solution is filtered will depend upon how the palladium is to be determined. In any event, reserve the filtrate and washings for recovery of their platinum content.

(*l*) DETERMINATION OF PALLADIUM

Palladium may be determined either by weighing its glyoxime compound or by igniting its glyoxime compound to metal. The method used depends, to a great extent, upon the quantity of palladium being handled. When the quantity is less than 0.1 g, it may be more convenient to determine the palladium as palladium dimethylglyoxime, but when the quantity exceeds 0.1 g, owing to the difficulty in filtering and washing the precipitate in a filtering crucible, it is preferable to determine it as metal.

If the palladium is to be determined as the glyoxime compound, catch the precipitate in a filtering crucible of either porcelain or glass, wash it first with warm diluted hydrochloric acid (1+99) and finally with warm water. Dry the precipitate at 110° C, weigh it, and calculate its palladium content, using the theoretical factor 0.3167.

If the palladium is to be determined as metal, catch the precipitate on paper, and, after washing, ignite it slowly in a porcelain crucible, first in air and then in hydrogen. Finally, ignite the residue in carbon dioxide for 2 minutes, cool it in an atmosphere of this gas, and weigh it as metallic palladium.

The palladium to be determined will consist of that portion which was recovered from the solution containing indium, copper, zinc, and nickel and the remaining portion which was recovered in the separation of palladium from rhodium and platinum, or from platinum alone.

If the palladium is to be determined as metal, ignite the two filters with their precipitates and finish the determination. If it is desired to determine palladium as its glyoxime compound, it is necessary to redissolve the small quantity of palladium dimethylglyoxime first obtained and to reprecipitate it. For this purpose use 5 ml of sulfuric acid, in the manner previously described, and precipitate the palladium from a volume of 100 ml. Finish the determination as directed.

(m) DETERMINATION OF RHODIUM

If the alloy contains rhodium, the procedure described for the collective separation of palladium and rhodium from platinum should be followed. The filtrate obtained in the subsequent single precipitation of palladium by dimethylglyoxime will contain all the rhodium in the alloy.

To recover rhodium, evaporate the filtrate from the precipitation of palladium, destroy with aqua regia the residual glyoxime contained in it, and decompose nitroso-compounds by evaporating with hydrochloric acid. It should be noted that residual glyoxime must be destroyed before attempting to precipitate the rhodium quantitatively with hydrogen sulfide. Add 10 ml of hydrochloric acid, dilute the solution somewhat, filter it, and wash the filter with diluted hydrochloric acid (1+99). Dilute the solution to a final volume of 200 ml,

heat it to boiling, and pass in a rapid stream of hydrogen sulfide for 30 minutes. Allow the solution to cool somewhat with the hydrogen sulfide still passing through it, to insure complete precipitation of the rhodium.

Catch the precipitate on a filter and wash with diluted hydrochloric acid (1+99). Ignite the dried filter and precipitate in a porcelain crucible, first in air and then in hydrogen. Allow the residue to cool in hydrogen and weigh it as metallic rhodium.

(n) DETERMINATION OF PLATINUM

All the platinum which the alloy contains will be found in the nitrite filtrates resulting from the collective precipitation of indium, copper, zinc, and nickel. After the removal of palladium and rhodium, it is recovered by precipitation with hydrogen sulfide.

If palladium and rhodium have been collectively separated from platinum by hydrolysis in a solution containing sodium bromate, add 20 ml of hydrochloric acid to each of the filtrates obtained from the precipitation of the dioxides of palladium and rhodium. Carefully warm the solutions until they become quiescent, partially concentrate them, combine them, and then evaporate to dryness. Make certain that all bromate is destroyed, by evaporating with hydrochloric acid. Add 20 ml of hydrochloric acid, dilute the solution to 200 ml, and filter it. Wash the filter with diluted hydrochloric acid (1+99). Finally, dilute the solution to about 400 ml, heat it to boiling, and pass in a rapid stream of hydrogen sulfide for 30 minutes. Allow the solution to cool somewhat with the hydrogen sulfide still passing through it, to insure complete precipitation of the platinum. Filter the solution and wash the precipitate with diluted hydrochloric acid (1+99).

If only palladium has been separated from platinum, by a repeated precipitation with dimethylglyoxime, evaporate the filtrate obtained in the second precipitation of palladium with glyoxime reagent. Destroy organic matter in it by adding nitric acid to the hot solution, and then evaporate until about 2 ml of sulfuric acid remains. Add 10 ml of diluted aqua regia, to redissolve any platinum which separates, and combine the resulting solution, without filtering it, with the filtrate obtained in the first precipitation of palladium with dimethylglyoxime. Evaporate the combined solutions, and destroy the glyoxime which it contains with nitric acid. Finally, repeatedly evaporate the solution with hydrochloric acid until oxides of nitrogen are no longer observed when the dried mass of salt is treated with hydrochloric acid. Dissolve the evaporated salt residue in 100 ml of water, filter the solution, wash the filter with diluted hydrochloric acid (1+99), add 10 ml of hydrochloric acid, and dilute to a final volume of 400 ml. Recover the platinum by precipitation with hydrogen sulfide as previously directed.

Ignite the dried filter and precipitate of platinum sulfide in a porcelain crucible. Leach the metallic residue with diluted hydrochloric acid (1+10), to extract sodium salts, transfer it to a filter, and wash it thoroughly with hot water. Ignite the filter and metal again in air, and weigh the residue as metallic platinum.

The metal so obtained will usually contain a small but significant amount of sulfur, the quantity of which ranges from 0.0 to 1.0 mg, with portions of platinum weighing 0.25 g. If the highest accuracy is

desired, dissolve in aqua regia the metallic platinum, obtained by ignition of the sulfide. Destroy nitroso-compounds by evaporating with hydrochloric acid, filter the solution into a clean, unetched beaker, and wash the filter with diluted hydrochloric acid (1+99). Dilute the solution to 100 ml, heat it to boiling, and add to it a solution containing 3 g of sodium acetate and 1 ml of formic acid for each 0.25 g of platinum. Boil the resulting solution gently until the precipitated metallic platinum is well coagulated and the supernatant liquid is colorless. Filter the solution and wash the metallic deposit with a hot 1-percent solution of ammonium chloride. Ignite the filter and residue. Leach and wash as previously directed, and ignite again. Weigh the final residue as metallic platinum, which will now be free from sulfur.

(o) DETERMINATION OF MANGANESE, IRON, ALUMINUM, AND MAGNESIUM

Although manganese and iron are quantitatively precipitated under the conditions specified for the collective precipitation of indium, copper, zinc, and nickel, this alkalinity is too great for the complete precipitation of aluminum and probably not great enough for that of magnesium. As these four metals are so rarely encountered in dental gold alloys, provision for their determination has not been made, but tests have shown that their presence in no way interferes in the procedure described. If occasion arises for determining them, it is recommended that a separate portion of the alloy be taken and that those metals which are precipitated by hydrogen sulfide in acid solution first be collectively removed. By operating on the resulting filtrate, the four metals in question can then be separated and determined by conventional methods.

(p) SUGGESTED SIMPLIFICATION OF THE PROCEDURE

The procedure which has just been given was designed to obtain the highest degree of accuracy and to include all the metals likely to be encountered in the analysis of dental gold alloys. In many instances a lower degree of accuracy may suffice for practical purposes, particularly when economy of time is an all-important factor. To meet this requirement, the procedure can be simplified to some extent. First of all, the procedure naturally becomes shortened through the absence of a number of metals in the particular alloy being analyzed. A further shortening can be made by eliminating certain steps, such as those involving reprecipitation.

With modern methods of refining the platinum metals, iridium and rhodium will not occur in most alloys, or will be present only to the extent of a few hundredths of a percent. Unless these two metals are added intentionally, the steps involving their separation and determination may usually be disregarded. At the present time only a few alloys contain indium. Unless the alloy is known to contain indium, the portion of the procedure dealing with its isolation and determination drops out. If indium is present and disregarded, a portion of it will be precipitated with the copper and the remainder of it with the zinc. Nickel is now less frequently added than formerly. Although aluminum made its appearance as an alloying constituent for a short time, its addition to dental gold alloys seems to have been abandoned. Manganese and magnesium have infrequently been found in the alloys, but ordinarily they are not regarded as alloying constituents. Iron is encountered only as an impurity.

The metals most commonly encountered are silver, gold, tin, copper, zinc, palladium, and platinum. Many alloys do not contain both palladium and platinum, and some contain neither. With alloys containing only silver, gold, copper, zinc, and nickel, the procedure is reduced to a very simple form. In the analysis of such an alloy, the procedure can be modified with respect to the end point at which the collective precipitation of base metals is made. If the nitrite filtrate from the collective precipitation is combined with the solution produced by redissolving the base metals, it will not be necessary to neutralize beyond the end point of xylenol blue. The combined solutions will contain all the copper, zinc, and nickel in the alloy.

As previously mentioned, the procedure can be further shortened by the deliberate elimination of steps involving reprecipitation. In this connection, however, it may not be advisable to dispense with the second precipitation of the tin, because of the variable amount of gold which may contaminate the first precipitate. The second precipitation of tin does not involve much time.

If the alloy contains palladium and platinum, time can be saved, at the expense of accuracy, by dispensing with the reprecipitation of the silver as chloride, the reprecipitation of the base metals, and the reprecipitation of palladium in its separation from platinum by dimethylglyoxime. Although no attempt was made to ascertain exactly the effect of eliminating these reprecipitations, a few observations were made during the development of the complete procedure. When 0.1 g of copper was hydrolytically precipitated at the end point of xylenol blue, and thus separated from a similar quantity of either palladium or platinum, the copper precipitate retained not more than 1 mg of the particular platinum metal. At the end point of thymol blue, the alkalinity specified in the procedure, a greater amount of palladium contaminated the collective base metal precipitate, but this was the result of decomposition of the complex nitrite of palladium, and provision for its recovery is made in the procedure.

The principal cause of contamination of the precipitate of palladium dimethylglyoxime by platinum, when these two metals are so separated, is the gradual reduction of quadrivalent platinum to bivalent platinum, which then forms a compound similar to that of palladium. As this reduction is favored by heating the solution, it is recommended that palladium be precipitated at room temperature. Under such conditions the amount of platinum retained probably is not much greater than about 1 mg.

It was found that the amount of gold which dissolved when the collective base metal precipitate was treated with hot diluted hydrochloric acid, as recommended in the procedure, ranged from 0.0 to about 1.5 mg, but usually did not exceed about 0.5 mg.

III. DEVELOPMENT OF THE PROCEDURE AND DISCUSSION OF THE EXPERIMENTS

In the following experiments the copper, zinc, tin, and aluminum used were those metals issued by the National Bureau of Standards as materials with standard melting points. The iron was likewise one of the Bureau's standard samples. The silver was stated to have a purity of at least 99.97 percent, and the gold, refined by the U. S. Assay Office, contained an extremely small amount of copper and

silver. The platinum, palladium, and rhodium, prepared at the National Bureau of Standards, were found to be free from impurities, by spectrochemical analysis. Likewise by spectrochemical analysis, the indium was found to contain not more than faint traces of impurities. The nickel used was that obtained from nickel sulfate of reagent quality which had a very low cobalt content.

The results of 33 experiments, performed in the development and testing of the procedure, are compiled in table 1, while additional experimental data are given in the text in connection with the discussion of these experiments.

TABLE 1.—*Results which illustrate the accuracy of the separations involved in the analysis of dental gold alloys*

Experiment	Silver		Tin		Gold		Indium		Copper		Zinc		Nickel		Palladium		Platinum	
	Taken	Recovered	Taken	Recovered	Taken	Recovered	Taken	Recovered	Taken	Recovered	Taken	Recovered	Taken	Recovered	Taken	Recovered	Taken	Recovered
	g	g	g	g	g	g	g	g	g	g	g	g	g	g	g	g	g	g
1			0.0555	0.0556			0.0100	0.0100										
2			.0525	.0525			.0100	.0101										
3			.0623	.0622			.0100	.0100										
4					0.1297	0.1298											0.1183	0.1183
5					.1196	.1196											.1129	.1129
6					.1175	.1174									0.1117	0.1116		
7					.1158	.1158									.1141	.1141		
8									0.1069	0.1068					.1092	.1095		
9									.1048	.1047					.1054	.1054		
10							.0100	.0102	.2064	.2064	0.0405	0.0404	0.0201	0.0201				
11							.0100	.0101	.2036	.2036	.0405	.0404	.0201	.0201				
12							.0100	.0101	.2024	.2025	.0405	.0405	.0201	.0201				
13	0.1367	0.1366	.0189	.0185	1.4108	1.4104	.0200	.0203	.2047		.0203		.0201	.0200	.0893	.0892	.0888	
14	.1339	.1338	.0208	.0203	1.4026	1.4022	.0200	.0200	.2037		.0203		.0201	.0200	.0928	.0927	.0926	
15	.1375	.1373	.0220	.0220	1.4006	1.4004	.0200	.0201	.2022		.0203		.0201	.0200	.0882	.0882	.0906	
16			.0839	.0839	.7023	.7023												
17			.0745	.0744	.6592	.6592												
18			.0750	.0749	.6910	.6911												
19									.2066	.2061	.0200	.0199	.0200	.0200				
20									.2002	.1993	.0200	.0199	.0700	.0200				
21									.2037	.2026	.0200	.0199	.0200	.0200				
22									.2022	.2017	.0200	.0199						
23									.2046	.2042	.0400	.0397						
24									.2017	.2018	.0200	.0199						
25									.2018	.2019	.0400	.0399						
26					1.6294	1.6295			.2076	.2078					.1246	.1248		
27					1.3825	1.3825			.2005	.2006					.1272	.1271		
28									.2065	.2066	.0200	.0199			.1073	.1073		
29									.2062	.2063	.0200	.0199			.1158	.1157		
30									.2035	.2037	.0200	.0198			.1060	.1059		
31					1.3980	1.3978	.0202		.2011		.0200		.0200		.1006	.1007	.1026	.1027
32					1.4202	1.4204	.0202		.2006		.0200		.0200		.1035	.1035	.1049	.1050
33					1.4138	1.4139	.0202		.2058		.0200		.0200		.1045	.1043	.1017	.1018

NOTE.—In experiments 19, 20, 21, 22, and 23 copper was determined electrolytically and the results are low. By treating the electrolyzed solutions with hydrogen sulfide, small black precipitates were recovered. In experiments 19, 20, and 21, after ignition in hydrogen, the residues weighed 0.4, 0.8, and 0.7 mg, respectively. In experiments 22 and 23 the small amount of copper was determined colorimetrically by comparison with known amounts of copper. The quantities found were 0.3 and 0.4 mg, respectively.

1. EXPERIMENTS ON THE SEPARATION AND DETERMINATION OF TIN

To avoid the introduction of acetate into the solution, the subsequent elimination of which may cause loss of gold, and to effect a separation from indium and iron, conditions were investigated for the hydrolytic precipitation of tin by controlling the acidity in other ways. It was found that tin is completely precipitated at an acidity not greater than about pH 1, from a boiling solution containing chlorostannic acid, the form in which tin exists when a dental gold alloy is dissolved in diluted aqua regia. Three experiments were made in which 0.1018, 0.0879, and 0.0782 g of tin, each quantity dissolved in 25 ml of diluted aqua regia, were precipitated by neutralizing with sodium bicarbonate the hot solutions, 150 ml in volume, to an end point established by means of quinaldine red and thymol blue. Quinaldine red changes from colorless to red at about pH 1 and thymol blue changes from red to orange at about pH 1.5. The end point chosen was that acidity at which each indicator was red. The solutions were boiled for 5 minutes, filtered, and the precipitates washed with hot water which was acidified with hydrochloric acid to a range between the end points of bromphenol blue (pH 4) and thymol blue (pH 1.5). The precipitates were ignited to stannic oxide, from which were calculated the quantities of tin 0.1024, 0.0886, and 0.0789 g, respectively. The positive errors may possibly be attributed to the retention of a small amount of sodium chloride. Of primary significance was the fact that no tin was detected in the hydrolytic filtrates.

Because the precipitate of stannic acid so obtained is liable to be slightly contaminated by other metals, a second precipitation is necessary. As a repeated precipitation at pH 1.5 did not appear to be sufficiently effective, conditions were investigated for the hydrolytic precipitation of tin by mere dilution and warming of solutions containing stannic sulfate in sulfuric acid, since the simplest and usual way of dissolving precipitates of stannic acid is by means of hot sulfuric acid. It was found that tin is completely precipitated from such solutions if the quantity of sulfuric acid does not exceed 5 ml in a volume of 100 ml (1.8 *N*). Three experiments were made in which 0.1054, 0.1087, and 0.1017 g of tin were taken. The solutions, each 200 ml in volume and containing 5 ml of sulfuric acid, were boiled for 5 minutes, then set on the steam bath for about 20 minutes, filtered, and the precipitates washed with hot water containing hydrochloric acid (pH 4 to 1.5). The quantities of tin recovered were 0.1055, 0.1088, and 0.1018 g, respectively, and no tin was detected in the filtrates and washings. The precipitate obtained by hydrolysis of stannic sulfate differs somewhat in character from that obtained by the hydrolysis of chlorostannic acid, and it has a tendency to adhere to the walls of the beaker. To avoid a tendency of the solution to bump when boiled, it is recommended in the final procedure that hydrolysis of the sulfate compound be accomplished by heating at the temperature of the steam bath (about 85° C) for 1 hour. It is further recommended, to avoid the remote possibility of a loss of tin when the precipitate is ignited, that washing be done with hot water acidified with sulfuric acid (pH 4 to 1.5).

The isolation of tin required a knowledge of the behavior of the other metals which were liable to contaminate the precipitate of stannic acid. Indium begins to precipitate as an opalescent colloid at an acidity slightly greater than pH 4, and is completely precipitated

between the limits pH 6 (end point of chlorphenol red) and about pH 10 (end point of thymolphthalein). To ascertain whether repeated precipitation of stannic acid from sulfate solution would eliminate indium, three experiments were made in which 0.1044, 0.1171, and 0.1000 g of tin were taken. The quantities of indium taken were 0.0988, 0.1166, and 0.1172 g, respectively. The tin was precipitated four times from a volume of 200 ml, containing 5 ml of sulfuric acid, and the precipitates were washed with hot water acidified with hydrochloric acid (pH 4 to 1.5). The quantities of tin recovered were 0.1045, 0.1177, and 0.0995 g, respectively. The amounts of indium recovered were 0.0994, 0.1165, and 0.1184 g. In these experiments the indium was recovered by precipitation with ammonium hydroxide and the precipitates were washed with a hot 1-percent solution of ammonium chloride neutral to bromcresol purple.

As the indium oxide so obtained is liable to be contaminated, three experiments were made in which 0.1214, 0.0886, and 0.1183 g of indium were taken and subsequently recovered by precipitation with hydrogen sulfide at room temperature. The indium was converted to indium sulfate and precipitated from 150 ml of solution, which was adjusted to an acidity of 0.02 *N* with respect to sulfuric acid. The sulfide precipitates were washed at room temperature with 0.01 *N* sulfuric acid and ignited at a temperature not above 1,000° C. The quantities of indium recovered were 0.1218, 0.0888, and 0.1186 g. In this connection it was of interest to ascertain whether a single precipitation of indium by hydrogen sulfide, according to the recommended procedure, sufficed to separate this metal from small amounts of iron and aluminum. In each experiment 0.0100 g of indium, 0.0045 g of iron, and approximately 4 mg of aluminum were taken. The recovery of aluminum was not attempted. The indium recovered in each instance was 0.0100 g, and the quantities of iron found in the filtrates, determined by titration with potassium permanganate, were 0.0044, 0.0045, and 0.0046 g.

To ascertain whether repeated precipitation of stannic acid from sulfate solution would eliminate iron, a single experiment was made in which 0.1186 g of tin and 0.1121 g of iron were taken. The tin was hydrolytically precipitated four times. The second filtrate contained 6 mg of iron, and the fourth, only a trace. The quantity of tin recovered was 0.1192 g, but the oxide was very slightly discolored. Two such precipitations of tin, in an experiment in which approximately 0.1 g of tin and 0.1 g of copper were taken, sufficed to eliminate copper. Only a very small amount of copper was detected in the second filtrate with potassium ferrocyanide, and no copper was detected in the filtrate obtained by dissolving the second tin precipitate and removing the tin by ammonium hydroxide.

Stannic acid, obtained by precipitation from a chloride solution containing gold, will always be contaminated by gold, and, if ignited, will be discolored. When the precipitate of stannic acid is dissolved in sulfuric acid and the resulting solution gently fumed, however, the gold which was adsorbed by the precipitate separates and agglomerates. If the solution of stannic sulfate is not diluted too much and is not allowed to become hot, it can be filtered and thus freed from gold, as well as from silica. If, on dilution, a purple colloid appears, the solution should again be digested at the fuming temperature of the sulfuric acid, in order to coagulate the colloidal gold.

In the case of a dental gold alloy, two precipitations of the tin, in the amounts usually encountered, were found to be sufficient to free it from contamination, provided the first precipitation is made from a chloride solution at about pH 1.5 and the second by diluting a sulfate solution containing 5 ml of sulfuric acid to a volume of 200 ml. The nine results given in table 1 under the heading "Tin" were obtained by following the recommended procedure. The errors in experiments 13 and 14 were the result of mechanical loss in attempting to recover a trace of gold, before this detail of the procedure was fully established.

2. EXPERIMENTS ON THE SEPARATION OF BASE METALS FROM GOLD AND THE PLATINUM METALS, AND OF THESE METALS FROM ONE ANOTHER

It was found that gold is precipitated as metal in well coagulated form by sodium nitrite from a chloride or aqua regia solution over a considerable range of acidity. At an acidity of pH 4 precipitation of gold did not appear to be quite complete, but at about pH 8, the end point of cresol red or of xylenol blue, it was found to be quantitative.

In experiments 4, 5, 6, and 7, gold was precipitated twice from acid solution, with final neutralization with sodium bicarbonate to the end point of cresol red. Washing was done with a hot 1-percent solution of sodium nitrite neutral to cresol red.

In experiments 8 and 9, copper and palladium were separated from each other under the conditions just described for the separation of gold from palladium and from platinum. Two experiments were also made in which copper was separated from platinum, but the recoveries of copper were low by 0.5 and 0.3 mg, respectively. In these experiments copper was recovered by precipitation as cuprous thiocyanate and ignited to metal. It was observed, in general, that errors up to about 1 mg were to be expected if this method of recovering copper were used. Copper could always be detected in the thiocyanate filtrates. It was found that the amount of palladium or of platinum which contaminated the first precipitate of copper under the conditions of these particular experiments did not exceed 1 mg.

As zinc and nickel likewise appeared to precipitate quantitatively in a solution containing sodium nitrite, it was necessary to provide for the subsequent separation of indium, copper, zinc, and nickel from one another. Experiments 10, 11, and 12 show the results obtained by following that part of the recommended procedure which deals with the separation of these four metals from one another. It was found experimentally that indium must be removed before precipitating copper with hydrogen sulfide. When 0.2 g of copper was precipitated, as directed in the procedure, from a solution also containing 10 mg of indium, the amount of indium which contaminated the precipitate of copper sulfide, and which was subsequently recovered from it, was 6.0 mg. In a similar experiment in which 20 mg of indium was added, the quantity of indium which accompanied the copper was 8.3 mg.

In experiments 13, 14, and 15, it was found that copper and zinc failed to precipitate quantitatively when the collective precipitation of the four base metals was made with sodium bicarbonate at the end point of cresol red. In these particular experiments, however, a considerable quantity of sulfuric acid, obtained from the reprecipitation of the tin, had been neutralized. As the effect of accumulated salts on sulfonphthalein indicators is such that, in general, the true pH

of the solution is less than that shown by the indicator, a series of three experiments in which copper, zinc, and nickel were precipitated by sodium bicarbonate, and a series in which they were precipitated by sodium hydroxide, were made. In both series, the quantity of accumulated salt was kept at a minimum. Neutralization was controlled to an end point between those indicated by cresol red and xylenol blue. Xylenol blue changes from yellow to blue just on the alkaline side of the color change of cresol red. Using approximately the same quantities of copper, zinc, and nickel as in experiments 13, 14, and 15, it was found that the errors in the copper determinations were 0.0000, −0.0003, and −0.0001 g in the bicarbonate series, and a trace of copper was detected in the hydrolytic filtrates. In the series with sodium hydroxide the errors were −0.0006, −0.0014, and −0.0011 g, but these were caused by faulty ignition of the copper sulfide precipitates rather than by incomplete precipitation, because no significant amount of copper was detected in the filtrates. In the bicarbonate series the error in each zinc determination was −0.0014 g; in the series with sodium hydroxide the errors were −0.0019, −0.0025, and −0.0009 g. Approximately these quantities of zinc were detected in the filtrates. There was no error in the nickel determination in the experiments using sodium hydroxide, and no significant amount of nickel was detected in the hydrolytic filtrates. In the bicarbonate series errors of as much as −0.0003 g were found and the corresponding filtrates showed a trace of nickel. Additional experiments in which approximately 0.1 g of zinc was precipitated by sodium hydroxide at the cresol red-xylenol blue end point, and only the filtrates investigated, showed definitely that precipitation of zinc was not complete and that quantities of zinc ranging from about 1.5 to 2.5 mg remained in solution.

It was found, however, that copper, zinc, and nickel were completely precipitated if the alkalinity of the solution was increased with sodium hydroxide to that corresponding to the end point of thymolphthalein, an indicator which changes from colorless to blue in the range pH 9.4 to 10.6. Neither copper nor zinc could be detected in the entire evaporated filtrates with either potassium ferrocyanide or potassium mercuric thiocyanate, under the appropriate conditions for such tests. Dimethylglyoxime revealed no nickel.

In experiments 19, 20, and 21, copper, zinc, and nickel were collectively precipitated twice at the end point of thymolphthalein and washed each time with about 100 ml of a 1-percent solution of sodium nitrite neutral to this indicator, at room temperature. It is to be noted that the copper was determined electrolytically and that the results are low. By treating the electrolyzed solutions with hydrogen sulfide, small black precipitates were recovered, which, when ignited, weighed 0.0004, 0.0008, and 0.0007 g, respectively.

Experiments 22, 23, 24, and 25 were accordingly made to compare the method of recovering copper electrolytically with that in which copper is precipitated as sulfide and ignited to metal. In these four experiments copper was first separated from zinc by precipitation with hydrogen sulfide as directed in the recommended procedure. The sulphide precipitates in experiments 24 and 25 were carefully ignited to oxide and reduced to metallic copper, whereas those in experiments 22 and 23 were redissolved and the copper was precipitated electrolytically. A small amount of copper was recovered from

the electrolyzed solutions by precipitation with hydrogen sulfide, but determined in this instance colorimetrically with potassium ferrocyanide in acetic acid solution by comparison with known amounts of copper. The amounts found were 0.3 and 0.4 mg, respectively.

To ascertain whether a significant amount of zinc contaminated the precipitates of copper sulfide, under the conditions of separation specified in the recommended procedure, the electrolyzed solutions in experiments 22 and 23, after removal of the small amounts of copper just mentioned, were evaporated until the sulfuric acid which they contained was eliminated. The residues were taken up in 10 ml of water, but the resulting solutions were not filtered. Potassium ferrocyanide produced a turbidity in each about comparable to that of 0.1 mg of zinc.

It was observed that when the base metals were precipitated by either sodium bicarbonate or sodium hydroxide, a sudden coagulation of the precipitate occurred at the cresol red-xylenol blue end point, leaving a clear mother liquor. The copper precipitate was usually bluish white with a slight tendency to darken on boiling. At this alkalinity the complex nitrites of palladium, platinum, rhodium, and iridium are stable and pass into the nitrite filtrates from the hydrolytic precipitates of the base metals, as was found to be true in experiments 4, 5, 6, 7, 8, 9, 13, 14, and 15.

When the precipitation of the base metals is made at the end point of thymolphthalein, however, the nitrite complex of palladium begins to decompose and deposit hydrated palladium oxide, so that palladium is not readily eliminated by repeated precipitation of the base metals but must be recovered from them by precipitation with dimethylglyoxime. It was found that the complex nitrates of platinum and of rhodium are stable at the end point of thymolphthalein and do not contaminate the base metal precipitate.

Some difficulty was encountered in using the indicator thymolphthalein, particularly if the solution contained considerable palladium. The indicator is readily soluble in alcohol, but not in water. In using this indicator a drop of a 1-percent solution of it in ethyl alcohol was added directly to the solution in which the precipitation was being made. The complex nitrite formed by 0.1 g of palladium imparts a rather intense yellow color which interferes with the judging of the end point by producing a green color with the indicator. Because of this the end point may be overrun, with the result that nearly all of the palladium will be precipitated. Furthermore, the character of the base metal precipitate obtained by boiling the solution at the end point of thymolphthalein differs from that obtained at the end point of cresol red-xylenol blue. The increase in alkalinity causes the precipitate to shrink noticeably and changes that formed by copper from blue to brown. The finely divided precipitate settles more slowly and interferes with the detection of the end point.

It was found that thymol blue, which is thymolsulfonphthalein, changes from yellow to blue at practically the same alkalinity as that at which thymolphthalein changes from colorless to blue, under the conditions which obtain in these analyses. As the sulfonphthalein compounds are soluble in water, dilute solutions of their monosodium salts furnish an easier means of establishing a desired pH by using them to test a drop of the solution which clings to the end of a stirring rod.

Experiments 26 to 33, inclusive, were made according to the recommended procedure. In each instance a small amount of palladium was recovered by dimethylglyoxime from the redissolved second precipitate of base metal. An amount of zinc not exceeding about 0.1 mg was detected with potassium ferrocyanide in the evaporated filtrates resulting from the precipitation of the main quantity of palladium in experiments 28, 29, and 30. In experiments 31, 32, and 33 no zinc was detected by hydrogen sulfide in the filtrates resulting from the removal of platinum. In these same experiments palladium was separated from platinum by two precipitations with dimethylglyoxime. In experiments 13, 14, and 15, palladium and platinum were first separated from each other by precipitating the palladium as its hydrated dioxide.

In experiments 13, 14, 15, 26, 27, 31, 32, and 33 the precipitate of base metals was separated from the precipitated gold by means of hot diluted hydrochloric acid, according to the recommended procedure. In this connection, it should be remarked, however, that danger of mechanical loss may result if the base metals have been precipitated as carbonates, because of effervescence. No danger attends the dissolving of a precipitate formed by sodium hydroxide. It was observed that an error ranging from -0.0002 to -0.0017 g, but usually about -0.0005 g, occurred in the determination of gold, and that these small quantities of gold appeared on the filter when the base metal precipitates were redissolved after the second precipitation. In the case of experiments 13, 14, 15, 31, 32, and 33, this small amount of gold was identified by dissolving it and precipitating it with sulfur dioxide. It was finally recovered by digestion with hot sulfuric acid. In experiments 26 and 27 the filter containing the trace of gold was ignited with that containing the bulk of gold, as in the recommended procedure.

The determination of silver offers no particular difficulty. In connection with its determination experiments were made to simplify the recovery of traces of palladium and platinum which contaminate the original precipitate of silver chloride, and which are converted to ammine-compounds when the silver chloride is dissolved in ammonium hydroxide. In one experiment 0.0146 g of platinum was dissolved in aqua regia; in the other, 0.1164 g of palladium. The solutions were made ammoniacal and boiled to convert these metals to the ammine-form. To each solution was added 5 ml of sulfuric acid and a few milliliters of nitric acid. The solutions were then heated to the fuming point of sulfuric acid for about 30 minutes. The amount of platinum recovered by precipitation with hydrogen sulfide was 0.0148 g. The amount of palladium recovered by precipitation with dimethylglyoxime, and determined as the glyoxime compound, was 0.1159 g. Each filtrate was heated for an additional 30 minutes at the fuming point of sulfuric acid, but the one yielded no precipitate upon further treatment with hydrogen sulfide, and the other, no precipitate with dimethylglyoxime.

IV. EXPERIMENTS ON THE BEHAVIOR OF OTHER BASE METALS

Under the conditions specified in the recommended procedure for the collective precipitation of indium, copper, zinc, and nickel, a number of other metals also appear to precipitate quantitatively. In

the following experiments, about 0.1 g of metal was taken and precipitated, from a solution containing nitrite and having a volume of 200 ml, at the blue end point of thymol blue. The time of boiling was 5 minutes, and the quantity of wash solution used was 100 ml of a 1-percent solution of sodium nitrite neutral to the indicator.

Cobalt, which forms a complex nitrite and is only partially precipitated at the end point of cresol red, produced a dirty brown precipitate. The filtrate and washings were separately evaporated to dryness with hydrochloric acid. In a volume of 15 ml, made slightly ammoniacal, hydrogen sulfide produced no precipitate in either instance. In a second experiment in which only the filtrate was investigated, an extremely faint dark precipitate was obtained with hydrogen sulfide, but, when it was dissolved in diluted aqua regia and the resulting solution evaporated to dryness with hydrochloric acid, no cobalt could be detected microchemically with potassium mercuric thiocyanate.

Bivalent manganese was precipitated in one experiment at the end point of thymolphthalein, and, in the other, at the end point of thymol blue. The filtrate and the wash water in the first experiment and the filtrate only in the second experiment were separately evaporated and tested with potassium periodate. Neither filtrate produced a color of permanganate. The wash solution developed a faint pink color which was not as intense as that produced by 0.05 mg of manganese.

Iron and tervalent chromium were likewise found to be quantitatively precipitated at the end point of thymol blue, but at this alkalinity a considerable amount of aluminum remained in solution. Although the behavior of cadmium and of bismuth was not thoroughly investigated, it appeared that neither metal was quite completely precipitated either at the end point of cresol red or of thymol blue.

It was not found possible to precipitate lead completely with sodium hydroxide at any alkalinity. However, a few experiments in which 0.1 g of lead, taken as lead chloride, was precipitated with sodium bicarbonate from a boiling solution containing nitrite, at the end point of xylenol blue, indicated the possibility of separating it from the platinum metals. In experiments in which only lead was taken, no lead was detected in the filtrates resulting from the precipitation with bicarbonate. The filtrates were tested by evaporating them to dryness with hydrochloric acid, diluting to 50 ml, and passing in a stream of hydrogen sulfide for 1 hour.

Three experiments were made in which 0.1123, 0.1089, and 0.1066 g of palladium were respectively separated from 0.1 g of lead by twice precipitating the lead with bicarbonate, in a solution containing nitrite, at the end point of xylenol blue. The precipitate in each instance was washed with about 100 ml of a 1-percent solution of sodium nitrite neutral to the indicator, at room temperature. Palladium was recovered by precipitation with dimethylglyoxime and determined as metal. The recoveries of palladium were 0.1122, 0.1088, and 0.1065 g, respectively. The precipitates of lead carbonate were dissolved in diluted hydrochloric acid, and the resulting solutions were evaporated to dryness. The dry residues of lead chloride were white. They were subsequently dissolved in 100 ml of water con-

taining 2 to 3 ml of hydrochloric acid and tested for palladium with dimethylglyoxime. No palladium was detected.

Four experiments were made in which 0.1126, 0.1041, 0.1142, and 0.1159 g of platinum were likewise respectively separated from 0.1 g of lead. Platinum was recovered by precipitation with hydrogen sulfide and the sulfide ignited to metal for determination. The metal residues were not reprecipitated to eliminate sulfur, and the recoveries were slightly high. The recovered metal weighed 0.1127, 0.1048, 0.1149, and 0.1162 g, respectively. The absence of platinum in the precipitates of lead carbonate was proved by dissolving the precipitates in hydrochloric acid, evaporating the solutions to dryness, and eliminating the lead by precipitating it with potassium iodide, in slight excess. The resulting mother liquors, even when filtered, were colorless.

In the preceding experiments, the metallic residues were not tested for lead. Additional experiments on the separation of lead from the platinum metals are in progress, and a complete report will be made in a subsequent paper.

V. ADAPTATION OF THE PROCEDURE TO THE REFINING OF CRUDE MATERIAL CONTAINING GOLD AND THE PLATINUM METALS

The procedure which has been given for the analysis of a dental gold alloy may be used, with slight modification, for recovering the precious metals in materials of the general type of dental gold scrap.

If it is to be so used, a few suggestions are in order. The procedure should be altered with respect to the conditions for precipitating gold and also for precipitating base metals. It was found experimentally that no gold was precipitated by nitrite in a solution containing 10 percent of concentrated hydrochloric acid by volume. At half of and at quarter of this acid concentration, gold is precipitated as well-coagulated, clean-looking metal which, when washed, is free from impurities. In separating the gold the acidity of the solution should not be allowed to become less than that corresponding to the end point of thymol blue (about pH 1.5). A small amount of gold will remain in solution but it is recoverable when the base metals are subsequently precipitated.

It is recommended that the base metals be precipitated with sodium hydroxide at the end point of xylenol blue (about pH 8), in order that the platinum metals shall pass entirely into the nitrite filtrates.

It is further recommended that platinum be separated from other platinum metals by hydrolytically precipitating the latter as hydrated oxides in a solution containing sodium bromate, at the end point of xylenol blue.

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PYRANOSE-FURANOSE INTERCONVERSIONS WITH REFERENCE TO THE MUTAROTATIONS OF GALACTOSE, LEVULOSE, LACTULOSE, AND TURANOSE[1]

By Horace S. Isbell and William W. Pigman

ABSTRACT

Mutarotation measurements at 20 and 0° C are reported for lactulose and turanose in buffered solutions at pH 4.6 and for galactose, glucose, and levulose at numerous points between pH 1 and 7. The mutarotation of levulose and the rapid mutarotation of galactose are extremely sensitive to the catalytic action of acids and bases and vary with pH in like manner. The mutarotation reactions of levulose, lactulose, and turanose differ fundamentally from the alpha-beta pyranose interconversions and resemble in all respects the rapid mutarotation reactions of sugars which contain the galactose, talose, and idose structures. Since the mutarotation of levulose is like that of the fructofuranose set free from sucrose by the action of invertase, but in the opposite direction, the mutarotation of levulose must consist in a pyranose-furanose interconversion. The conclusion that the mutarotation of levulose results from a pyranose-furanose interconversion leads to the following important deductions: (1) That the mutarotation of lactulose is caused by a furanose-pyranose change and that crystalline lactulose is a furanose; (2) that the mutarotation of Hibbert's 1,3,4-trimethyl-fructofuranose results from a furanose-pyranose change and that the sugar is properly classified as a furanose; (3) that the mutarotation of turanose is due to a pyranose-furanose change and therefore the glucosido group is not united with the fifth or sixth carbon, but in all probability it is united with the third carbon; (4) that the rapid reactions characteristic of the complex mutarotations of galactose and other sugars are pyranose-furanose interconversions and that the complex mutarotations arise from the establishment of an equilibrium between the furanose and the normal alpha and beta pyranoses.

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[1] This paper was read before the Division of Sugar Chemistry and Technology of the American Chemical Society at Dallas, Tex., April 1938.

I. THE SUGARS IN SOLUTION

The determination of the composition of sugar solutions is a problem of great complexity because the sugars in solution readily change from one modification to another. By direct acetylation under different conditions, no less than five isomeric penta-acetates can be obtained for most sugars and by treatment with methyl alcohol containing hydrogen chloride, methyl pyranosides, and methyl furanosides are obtained. For these and other reasons, it seems probable that an equilibrium is established between the open chain and the alpha and beta pyranose and furanose modifications. But undoubtedly the system is more complex and various hydrated, enolic, and ionized forms take part in the equilibrium. The course of the mutarotation reactions, and the solubilities, rates of oxidation, and other properties of the sugars clearly show that the proportions of certain modifications are so small that they cannot be detected by direct methods. Extensive investigations [1, 2, 3][2] have shown that sugars containing the glucose, mannose, and gulose structures exist in solution almost completely as the normal alpha and beta isomers. Furthermore, the correlation of the optical rotations of the alpha and beta methyl-pyranosides with the alpha and beta normal sugars [4, 5, 6], together with the observation that the alpha and beta normal sugars are oxidized directly to delta lactones [7, 8], shows that the normal sugars are pyranoses and consequently the equilibrium solutions of glucose and similar sugars consist for the most part of the alpha and beta pyranoses. Hence the mutarotation reaction of α- and β-*d*-glucose principally results from the interconversion of the alpha and beta pyranoses [1, 2]. The mutarotation of sugars containing the galactose, talose, and idose structures, on the other hand, consists in a slow reaction, the interconversion of the alpha and beta pyranoses, accompanied by a rapid reaction, the conversion of the normal pyranoses to labile modifications and the interconversion of these labile modifications. Although the latter reaction is more complex, for convenience it can be considered as a single rapid reaction and the equilibrium can be treated as a three-membered system. The mutarotations of α- and β-*d*-glucose [2], α- and β-*d*-mannose [2, 9], β-*d*-allose [10], α-*d*-gulose $CaCl_2.H_2O$ [2, 11], α-*d*-xylose [2, 12], α- and β-*d*-lyxose [2], α-*d*-α-galaheptose [3], β-*d*-α-glucoheptose [3], β-*d*-β-galaheptose [3, 15], α- and β-lactose [2], β-maltose [2], and α- and β-*d*-4-glucosidomannose [16], follow, within experimental error, the equation for a first-order reversible reaction. On the other hand, the mutarotations of α- and β-*d*-galactose [2, 17, 18, 19], α- and β-*d*-talose [2, 20], α-*l*-arabinose [2, 21], β-*l*-arabinose $CaCl_2.4H_2O$ [2, 22], *l*-ribose [2, 23], mannose $CaCl_2.4H_2O$ [2, 24], α- and β-*d*-α-mannoheptose [3], α-*d*-β-guloheptose [3], *d*-β-glucoheptose [25], α-*d*-β-mannoheptose [26], and α-*d*-α-guloheptose [26, 27] are complex and for expression require an equation containing two exponential terms.

The labile constituents in the solutions of galactose and most aldoses are present in such small quantities that, although since the time of Pasteur many mutarotation measurements have been made, the existence of the rapid reaction was not definitely recognized until 1926 [17]. Hydration and the formation of ions occurs very rapidly and can be excluded as possible explanations for the rapid mutarotation

[2] Figures in brackets here and elsewhere in the text correspond to the numbered references at the end of this paper.

reactions. Although enolization occurs in alkaline solutions, it does not take place to an appreciable extent in acid solutions, and hence it cannot be used to explain a reaction which occurs to approximately like degree over a wide pH range. The absorption spectra, reactions, and properties of the sugars in solution demonstrate that the open-chain modifications are present in minute quantities only. Obviously these cannot be the labile substances responsible for the rapid mutarotations. This reasoning by elimination leaves the furanoses to account for the rapid mutarotation reactions. Despite the fact that it has been tacitly assumed that the constituents responsible for the rapid mutarotation are either the free aldehyde or furanose modifications, there has been no proof previous to this paper that the labile substances are either of these.

Several mechanisms for the rapid reactions may be postulated and subjected to mathematical analysis, but this procedure is of questionable value until more information is at hand regarding the substances which take part in the reactions. The rapid reactions may be caused by the interconversion of the alpha and beta furanoses or by a shift in the oxygen ring. In support of the latter hypothesis, it will be recalled that when mannose $CaCl_2.4H_2O$ is dissolved in water a rapid reaction occurs at a rate comparable to the rapid reactions of galactose, talose, and similar sugars and that the freshly dissolved sugar on bromine oxidation [28] yields largely mannonic γ-lactone with only a small quantity of mannonic δ-lactone, but that as the rapid mutarotation reaction proceeds the yield of γ-lactone decreases and the yield of δ-lactone increases. This is evidence that the rapid mutarotation reaction of mannose $CaCl_2.4H_2O$ consists in the change of the furanose to the pyranose modification.

It has been demonstrated by Hudson, Lowry, and others [29] that the mutarotations of sugars which establish equilibrium between two modifications follow the equation for a first-order reversible reaction. But, as shown by Riiber and Minsaas [17], Smith and Lowry [18], and others, the mutarotation of the sugars which establish equilibrium with substantial proportions of three or more modifications requires for expression a complex equation of the type

$$[\alpha]_D = A\,10^{-m_1 t} + B\,10^{-m_2 t} + \ldots\ldots + C \qquad (1)$$

The experimental observation that the mutarotations of certain sugars can be expressed by one exponential term, such as might be anticipated for two substances in dynamic equilibrium, while the mutarotations of other sugars require for expression two exponential terms, such as might be anticipated for three substances in dynamic equilibrium, does not necessitate that the mutarotations in the two groups be entirely different. Probably, in the first group, the changes caused by the formation of the labile isomers are much less than the errors of observation. Nor does the application of the equation containing two exponential terms signify that the system contains only three isomers but rather that the proportions of other isomers are small or that the velocity constants are not favorable for the detection of the changes. The mutarotation constant for the slow reaction is designated as m_1, and the constant for the rapid reaction is designated as m_2. The constant, m_1, is essentially the same as the "mutarotation coefficient", k_1+k_2, but m_2 is more or less empirical and represents the rapid reactions that cause the deviations in the mutarota-

tions of many sugars. It is not a true velocity constant but rather a function of the constants representing the rates of formation and alteration of the more labile modifications of the sugar in solution. Comparisons of the two reactions, represented by m_1 and m_2, under various conditions have shown that each reaction has characteristic properties which can be used to determine to which class it belongs. The nature of these distinctive properties will be developed in the following sections.

II. COMPARISONS OF THE MUTAROTATIONS OF LEVULOSE AND GALACTOSE

The relative extent of the two mutarotation reactions differs widely for the various sugars, but shows marked parallelism for sugars of similar structure. Sugars containing the galactose structure give complex mutarotations which reveal the existence of a characteristic rapid reaction. Fischer's projectional formula reveals that the pyranose modification of *d*-fructose [3] or levulose could be structurally related to either *α-l*-galactose or to *β-d*-allose. Since the optical rotation of levulose is in accord with the *α-l*-galactose structure [3, page 513], it is of interest to ascertain whether the mutarotation of levulose is like that of *α-l*-galactose. Although the mutarotation of levulose had been investigated extensively [31, 32, 33] we made new measurements to be sure that small deviations had not been overlooked and to obtain comparable data for levulose, galactose, and glucose. The results of these measurements are given in table 11, page 793. Much to our surprise the mutarotation of levulose, even at low temperatures, fails to give any evidence of the complex changes characteristic of the mutarotation of *α-d*-galactose. But, as will be shown in the next paragraph, the mutarotation of levulose is remarkably similar to the rapid mutarotation reaction of galactose and differs fundamentally from the alpha-beta pyranose interconversion.

In previous publications we have shown that the equilibrium proportions of the constituents involved in the rapid mutarotation reactions vary with temperature changes [30], whereas the equilibrium proportions of the alpha and beta pyranoses do not vary widely with temperature. It has been known for a long time that the optical rotation of levulose varies with temperature and that when the temperature of a levulose solution is changed a mutarotation occurs. As shown by Hudson's measurements, and confirmed by us, when a solution of levulose is cooled the resulting thermal mutarotation occurs at the same rate as the mutarotation of the freshly dissolved sugar (see table 9, page 791). The direction of the change shows that lowering the temperature shifts the equilibrium towards the more levorotatory modification, namely, the form known in the crystalline state. According to the Le Chatelier-Braun principle the direction of the shift caused by a lowering of the temperature indicates that heat is liberated by the conversion of the less levorotatory modification to the more levorotatory substance (levulose). This is in agreement with the energy measurements of Riiber and Esp [33] who showed that in the reverse reaction (the mutarotation of freshly dissolved levulose) heat is absorbed. These mutarotations and energy changes are similar to those found for galactose. As we noted in a previous publication

[3] The modification of *d*-fructose, which gives an initial specific rotation of −133°, will be called levulose in this paper—it is called *β-d*-fructose by Hudson and *α-d*-fructose by Isbell.

[2, page 163] when a solution of *d*-galactose is cooled the optical rotation increases rapidly to a maximum and then decreases slightly. The initial increase in optical rotation shows that the equilibrium is shifted from the labile modifications towards the alpha pyranose. Such being the case, the direction of the equilibrium shift is the same for galactose as for levulose, and the energy content of *α-d*-galactopyranose must be less than that of its labile modification. This is in accord with the work of Riiber and Minsaas [17] who reported that the temperature of a freshly prepared solution of *α-d*-galactose falls at first, passes a minimum, and then rises. The initial decrease in temperature which accompanies the rapid mutarotation reaction is evidence of the absorption of heat and corresponds to the decrease in temperature which accompanies the mutarotation of levulose.

The correlation of the rapid mutarotation of *α-d*-galactose and the mutarotation of levulose receives additional confirmation by the changes in volume and refractivity which occur during the respective mutarotation reactions. It was shown by Riiber and Minsaas [17] that a freshly prepared solution of *α-d*-galactose expands during the first 15 minutes at 20° C and then contracts. Since the expansion occurs at approximately the same rate as the rapid mutarotation, in all probability it is caused by the conversion of *α-d*-galactose to the labile modifications. A freshly prepared solution of levulose also expands during the first 15 minutes at 20° C. As shown by Riiber and Esp [33] the rate of expansion agrees with the rate of mutarotation and is clearly due to the same reaction. The striking similarity between the rapid reaction of galactose and the mutarotation reaction of levulose is illustrated further by a comparison of Riiber and Esp's measurements of molecular refraction for freshly prepared levulose solutions with those made by Riiber and Sørensen [36] for galactose. Riiber and Sørensen report that when *α-d*-galactose is dissolved in water the molecular refraction increases with the rapid mutarotation reaction, while Riiber and Esp report that when levulose is dissolved in water the molecular refraction increases at a rate comparable to that of the mutarotation reaction. The comparisons which have been cited bring out the marked similarity of the mutarotation of levulose and the rapid mutarotation of *α-d*-galactose; in the next section it will be shown that the mutarotation of levulose is like the other rapid mutarotation reactions and differs from the normal alpha-beta pyranose interconversion.

III. CLASSIFICATION OF THE MUTAROTATION REACTIONS

The rapid mutarotation reactions have certain characteristics which distinguish them from the normal alpha-beta pyranose interconversions. One of these, the effect of temperature on the equilibrium, has been considered already and found to support the classification of the mutarotation of levulose with the rapid reactions. The effect of temperature on the mutarotation rates, m_1 and m_2, also affords a means of classification. Previous measurements in this laboratory with many sugars have shown that the heats of activation obtained from the temperature coefficients for the rapid reactions involving the labile modifications are less than the heats of activation for the alpha-beta pyranose interconversions. In order to determine whether the heat of activation for the mutarotation of levulose agrees with the heat of activation for the rapid or for the slow reaction, mutarotation

measurements were made at 20 and 0° C under the usual conditions in ordinary distilled water. Check determinations gave velocity constants which differed by more than what appeared to be a reasonable experimental error. Further investigation revealed that the discrepancy was caused by variations in the carbon dioxide content of the water used for dissolving the sugar. This difficulty was overcome by making the measurements in the presence of an acid-base buffer. The results so obtained are reported in table 1.

TABLE 1.—*Effect of temperature on rate of mutarotation*

Sugar	t_1	t_2	Slow change			Rapid change			pH
			$m_1\times10^3$ at t_1	$m_1\times10^3$ at t_2	Q [a]	$m_2\times10^3$ at t_1	$m_2\times10^3$ at t_2	Q	
	°C	°C							
α-d-Glucose	20.05	0.10	6.48	0.766	17,000				4.6
α-d-Galactose	20.05	[b].15—(.30)	8.26	.969	17,300	73.6	11.9	14,600	4.6
β-d-Galactose	20.50	.20	8.51	.995	17,600	78.5	12.1	14,700	4.6
Levulose	20.05	.00				59.2	9.03	14,900	4.6
Turanose	20.70	.20				86.1	13.6	14,400	4.6
Lactulose	20.00	.10				43.5	6.04	15,800	4.6

[a] $2.3026\log\frac{k_1}{k_2}=\frac{Q}{1.9864}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$.

[b] The temperature during the rapid reaction was +0.15°, but during the slow reaction it rose to +0.30° C.

The heats of activation obtained for the mutarotations of levulose (14,900), turanose (14,400), and lactulose (15,800) are in agreement with the heat of activation for the rapid mutarotation reaction of galactose (14,600). These values are in accord with the values of 12,000 to 15,000 previously found for the rapid mutarotation reactions of other sugars and differ from the values 16,000 to 18,000 previously found for the alpha and beta pyranose interconversions.

For a long time it has been known that the rate of the mutarotation of levulose is particularly sensitive to small changes in acidity [31, 32]. To ascertain whether the rapid mutarotation reaction of galactose is likewise particularly sensitive to acid and basic catalysts we conducted a series of measurements on galactose, levulose, and glucose under strictly comparable conditions. The results of these measurements and other work has shown that the rapid mutarotations in general are much more sensitive to acid and basic catalysts than the normal alpha-beta pyranose interconversions. The results obtained by measurements in solutions of different acidity are summarized in tables 2 and 3, while the curves given in figures 1 and 2 illustrate graphically the marked difference in the effect of the catalysts on the two reactions. Notice in figures 1 and 2 that the normal mutarotations of galactose and glucose remain nearly constant from pH 3 to pH 6, while the rates for the mutarotation of levulose and the rapid mutarotation of galactose rise much more rapidly on either side of pH 4. The effect of hydrogen and hydroxyl ions on the velocity constants for glucose at 25° C was found by Hudson [37] to follow an equation of the following type

$$m=A+B[H^+]+C[OH^-] \qquad (2)$$

TABLE 2.—*Effect of acids and bases on the mutarotation constants at 20° C.*

Buffer used	m	pH	$[H^+]$	$[OH^-]$ [a]	Equation calculated by assumption that:
α-d-Glucose. $m=0.0060+0.18\,[H^+]+16{,}000\,[OH^-]$					
0.001 *M* succinic acid	0.0060	3.70	2.00×10^{-4}	3.47×10^{-11}	$m=A$
o-Nitrophenol buffer 2	.0069	6.91	1.23×10^{-7}	5.62×10^{-8}	$m=A+C[OH^-]$
0.01 *N* HCl	.0079	1.98	1.05×10^{-2}	6.61×10^{-13}	$m=A+B[H^+]$
α-d-Galactose (slow reaction). $m=0.0081+0.35\,[H^+]+17{,}800\,[OH^-]$					
0.001 *M* KH phthalate	0.0081	4.41	3.89×10^{-5}	1.78×10^{-10}	$m=A$
o-Nitrophenol buffer 2	.0091	6.91	1.23×10^{-7}	5.62×10^{-8}	$m=A+C[OH^-]$
0.01 *N* HCl	.0117	1.99	1.02×10^{-2}	6.76×10^{-13}	$m=A+B[H^+]$
α-d-Galactose (fast reaction). $m=0.069+9.7\,[H^+]+1{,}370{,}000\,[OH^-]$					
0.001 *M* KH phthalate	0.069	4.41	3.89×10^{-5}	1.78×10^{-10}	$m=A$
o-Nitrophenol buffer 2	.146	6.91	1.23×10^{-7}	5.62×10^{-8}	$m=A+C[OH^-]$
0.01 *N* HCl	.168	1.99	1.02×10^{-2}	6.76×10^{-13}	$m=A+B[H^+]$
Levulose. $m=0.055+7.3\,[H^+]+1{,}570{,}000\,[OH^-]$					
0.001 *M* KH phthalate	0.055	4.42	3.80×10^{-5}	1.82×10^{-10}	$m=A$
o-Nitrophenol buffer 2	.145	6.92	1.20×10^{-7}	5.75×10^{-8}	$m=A+C[OH^-]$
0.01 *N* HCl	.133	1.97	1.07×10^{-2}	6.46×10^{-13}	$m=A+B[H^+]$

[a] Calculated from the pH measurement by use of the expression, $\log[OH^-]=-14.16+pH$. The value for the ion product of water at 20° C is taken as $10^{-14.16}$ (Int. Crit. Tables 6, 152 (1929)).

TABLE 3.—*Summary of mutarotation constants obtained in buffered aqueous solutions of different acidity*

pH ±0.05	Solvent [1]	Temperature ±0.05° C	Velocity constant m	m [2] corrected to 20° C	Ratio [3]
α-d-Glucose					
1.05	0.1 *N* HCl	20.00	0.0230	0.0230	3.57
1.98	0.01 *N* HCl	20.05	.00797	.00793	1.23
2.37	0.004 *N* HCl	20.20	.00705	.00691	1.07
3.03	0.001 *N* HCl	20.30	.00670	.00650	1.01
3.70	0.001 *M* succinic acid buffer 2	20.00	.00598	.00598	0.93
3.80	Approx. 0.1 *M* succinic acid buffer 1	20.00	.00765	.00765	1.19
4.60	KH phthalate buffer 2	20.05	.00648	.00645	1.00
5.57	KH phthalate buffer 3	20.25	.00688	.00671	1.04
5.57	KH phthalate buffer 3	20.20	.00680	.00666	1.03
6.13	KH phthalate buffer 4	20.00	.00679	.00679	1.05
6.45	KH phthalate buffer 5	20.05	.00692	.00689	1.07
6.43	*o*-Nitrophenol buffer 1	20.20	.00672	.00658	1.02
6.91	*o*-Nitrophenol buffer 2	20.25	.00709	.00692	1.07

[1] For the composition of the buffer solutions used, see table 8, page 790.

[2] The Arrhenius equation and the value of Q given in table 1 were used for converting the velocity constants to the standard temperature, 20° C.

[3] Ratio of velocity constant at the pH indicated to that at pH=4.6, the latter measured in 0.005 *N* potassium acid phthalate buffer solution 2.

TABLE 3.—*Summary of mutarotation constants obtained in buffered aqueous solutions of different acidity*—Continued

pH ±0.05	Solvent	Temperature ±0.05° C	Velocity constant m	m corrected to 20° C	Ratio
	Levulose				
1.04	0.1 *N* HCl	20.00	0.710	0.710	12.01
1.97	0.01 *N* HCl	20.05	.134	.133	2.25
2.37	0.004 *N* HCl	20.20	.0893	.0878	1.49
2.99	0.001 *N* HCl	20.00	.0627	.0627	1.06
4.04	KH phthalate buffer 1	20.70	.0602	.0564	0.96
4.42	0.001 *M* KH phthalate buffer 6	20.00	.0548	.0548	.93
4.61	KH phthalate buffer 2	20.35	.0612	.0593	1.00
4.57	KH phthalate buffer 2	20.05	.0592	.0589	1.00
5.54	KH phthalate buffer 3	20.25	.0880	.0861	1.46
5.64	KH phthalate buffer 3	20.20	.0866	.0851	1.44
6.11	KH phthalate buffer 4	20.05	.102	.102	1.73
6.45	KH phthalate buffer 5	20.05	.114	.114	1.93
6.92	*o*-Nitrophenol buffer 2	20.25	.148	.145	2.45
	α-*d*-Galactose (slow reaction)				
1.07	0.1 *N* HCl	20.00	0.0466	0.0466	5.67
1.99	0.01 *N* HCl	20.05	.0118	.0117	1.42
2.36	0.004 *N* HCl	20.20	.00963	.00944	1.15
3.04	0.001 *N* HCl	20.00	.00841	.00841	1.02
4.41	0.001 *M* KH phthalate buffer 6	20.05	.00817	.00813	0.99
4.55	KH phthalate buffer 2	20.05	.00826	.00822	1.00
5.57	KH phthalate buffer 3	20.20	.00849	.00832	1.01
5.7–6.2	$NaHCO_3$ buffer 1	20.00	.00819	.00819	1.00
6.09	KH phthalate buffer 4	20.00	.00851	.00851	1.04
6.45	KH phthalate buffer 5	20.00	.00874	.00874	1.06
6.91	*o*-Nitrophenol buffer 2	20.25	.00936	.00912	1.11
	β-*d*-Galactose (slow reaction)				
4.67	KH phthalate buffer 2	20.50	0.00851	0.00808	.....
	α-*d*-Galactose (rapid reaction)				
1.99	0.01 *N* HCl	20.05	0.169	0.168	2.29
2.36	0.004 *N* HCl	20.20	.130	.128	1.75
3.04	0.001 *N* HCl	20.00	.0846	.0846	1.15
4.55	KH phthalate buffer 2	20.05	.0736	.0733	1.00
5.57	KH phthalate buffer 3	20.20	.0886	.0871	1.19
5.7–6.2	$NaHCO_3$ buffer 1	20.00	.0951	.0951	1.30
6.09	KH phthalate buffer 4	20.05	.110	.110	1.50
6.45	KH phthalate buffer 5	20.05	.133	.132	1.80
6.91	*o*-Nitrophenol buffer 2	20.25	.149	.146	1.99
4.41	0.001 *M* KH phthalate buffer 6	20.05	.0697	.0694	0.95
	β-*d*-Galactose (rapid reaction)				
4.67	KH phthalate buffer 2	20.50	0.0785	0.0752	.....

Reduction of the results reported in table 2 to equations of like form, using the velocity constants in 0.01 *N* HCl for the determination of *B*, and the velocity constants in the presence of the *o*-nitrophenol buffer 2 for the determination of *C*, gives the following expressions:

Glucose at 20° C, $m_1=0.0060+.18\ [H^+]+16{,}000\ [OH^-]$
Galactose at 20° C, $m_1=0.0081+.35\ [H^+]+17{,}800\ [OH^-]$
Galactose at 20° C, $m_2=0.069+9.7\ [H^+]+1{,}370{,}000\ [OH^-]$
Levulose at 20° C, $m_2=0.055+7.3\ [H^+]+1{,}570{,}000\ [OH^-]$

Although these expressions are strictly comparable one to the other, they are arbitrary because they are based on measurements made in buffered solutions containing anions of weak acids. The work of Lowry and Smith [29], Kuhn and Jacob [38], Brönsted and Guggenheim [39], and others shows that the anions of weak acids and the molecules of undissociated strong acids have marked catalytic effects.

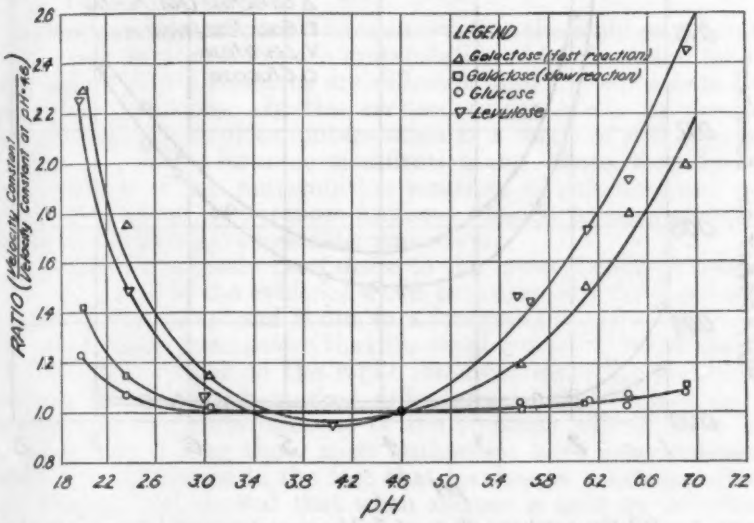


FIGURE 1.—*Variation of mutarotation constants with acidity.*

But on account of the difficulty of maintaining uniform conditions in unbuffered solutions, buffers were used by us even though their use complicates the problem by introducing another variable. A description of the buffers and a summary of the results are given on page 790 of this paper, while in figures 1 and 2 the results are represented in the form of curves. As clearly shown by the numerical equations and the curves of figures 1 and 2, the catalytic effects of the hydrogen and hydroxyl ions are much larger for the fast reactions than for the normal slow reactions. This difference is characteristic and serves to differentiate between the two reactions. The experimental results as expressed by the equations require minimum values at hydrogen-ion concentrations of 2.5×10^{-5}, 3.9×10^{-5}, 1.9×10^{-5}, and 3.2×10^{-5} for the mutarotation constants of glucose, levulose, and the slow and fast reactions of galactose. These correspond to the pH values of 4.61, 4.41, 4.73, and 4.50, respectively. The differences in the minimum points, however, are not sufficient to be characteristic properties.

Aside from showing the similarity in the mutarotation of levulose

to the rapid mutarotation reactions of galactose the results so far obtained emphasize the necessity of closer control of acidity in the measurements of the complex reactions. Because the rate of mutarotation of glucose is nearly constant over relatively wide changes in acidity, carbohydrate chemists have grown careless in the control of pH in mutarotation measurements. For sugars exhibiting rapid mutarotation reactions (ketoses and certain aldoses) this frequently leads to large variations in the results. Thus if the mutarotation measurements are made in freshly boiled water substantially free from carbon dioxide, much higher constants are obtained than if the measurements are made in ordinary water, which always contains carbon dioxide. A few results obtained with different samples of

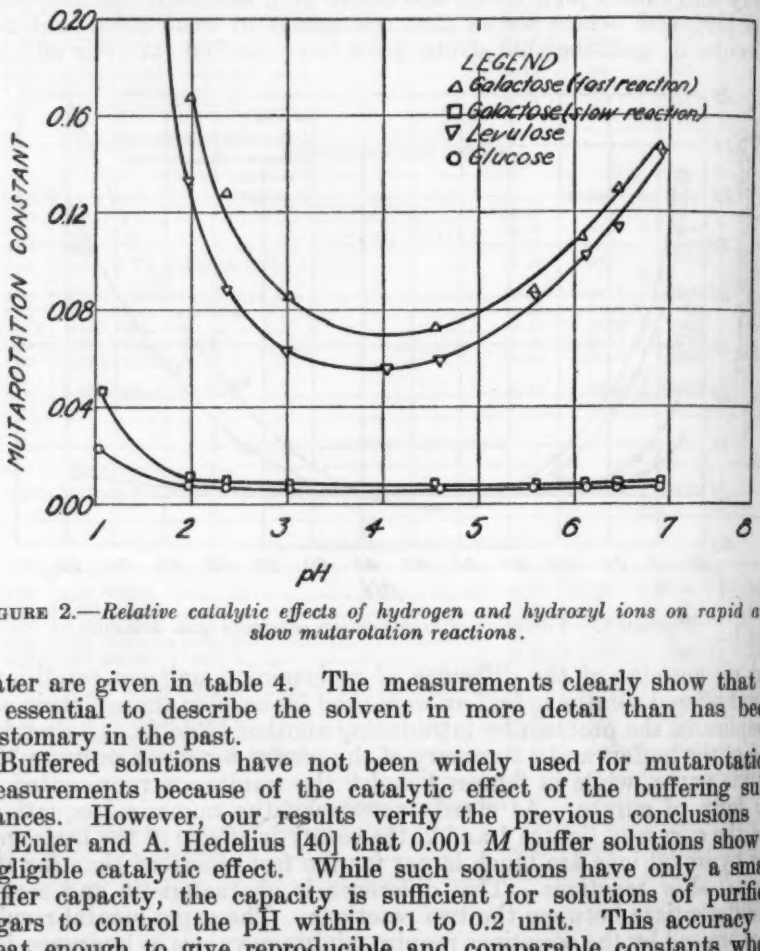


FIGURE 2.—*Relative catalytic effects of hydrogen and hydroxyl ions on rapid and slow mutarotation reactions.*

water are given in table 4. The measurements clearly show that it is essential to describe the solvent in more detail than has been customary in the past.

Buffered solutions have not been widely used for mutarotation measurements because of the catalytic effect of the buffering substances. However, our results verify the previous conclusions of H. Euler and A. Hedelius [40] that 0.001 *M* buffer solutions show a negligible catalytic effect. While such solutions have only a small buffer capacity, the capacity is sufficient for solutions of purified sugars to control the pH within 0.1 to 0.2 unit. This accuracy is great enough to give reproducible and comparable constants when the hydrogen ion concentration is near that for which the minimum rate of mutarotation is observed. Pure potassium acid phthalate is easily obtained (National Bureau of Standards Standard Sample 84), and since 0.001 *N* solutions are readily prepared and have a pH of about 4.4 at 20° C (which is near that for the minimum mutarotation value), we suggest that this solution be used as the solvent when

mutarotation measurements are made on new sugars so that ultimately a comparable set of mutarotation constants will be established for all sugars.

TABLE 4.—*Differences in mutarotation constants obtained in freshly boiled and ordinary distilled water*

Sugar	Distilled water	$m_1 \times 10^3$	$m_2 \times 10^3$	Sugar	Distilled water	$m \times 10^3$
α-d-Galactose	Ordinary	8.0	79	Levulose	Ordinary	54
Do	Boiled	8.4	108	do	Boiled	115
α-d-Talose	Ordinary	26.3	126	Turanose	Ordinary	77
Do	Boiled	43.3	248	do	Boiled	110

IV. EVIDENCE THAT THE MUTAROTATION OF LEVULOSE IS A PYRANOSE-FURANOSE INTERCONVERSION

In the previous sections we have shown that the rapid mutarotation reaction of galactose is like the mutarotation of levulose, and that the rapid mutarotation reactions are different from the alpha-beta pyranose interconversions. In this section, evidence will be presented showing that the levulose mutarotation is a result of a change from the pyranose to the furanose modification and, hence, that the complex character of the mutarotation reactions of galactose and other aldoses is due to a pyranose-furanose change accompanying the normal alpha-beta pyranose interconversion.

Reference has already been made to the mutarotation of mannose $CaCl_2.4H_2O$ and to the evidence which indicates that the rapid mutarotation of this compound is due to a furanose-pyranose interconversion. It has also been shown that the rapid mutarotation of mannose $CaCl_2.4H_2O$ is similar to the rapid mutarotations of galactose and levulose. Even though marked differences in the mutarotation of levulose and the mutarotations of the common aldoses have been recognized for a long time, most authorities have been content to ascribe the differences to the fact that levulose is a ketose. But in 1909 Hudson [41] showed that when sucrose is split by invertase a form of fructose is liberated which mutarotates at the same rate as levulose, but in the opposite direction, and in 1930 he stated [42] that "the measurements furnish clear proof that the initially liberated fructose is indeed a beta form but that it shifts its ring during the mutarotation." This important deduction was somewhat obscured by the fact that Hudson at that time assigned a 2,4 ring to the fructose constituent of sucrose. It is now generally accepted [43] that the fructose constituent of sucrose is a furanose and that normal fructose or levulose is a pyranose. Obviously the mutarotation reported by Hudson is caused by the conversion of the freshly liberated fructofuranose to levulose. In other words, the reaction consists in the partial conversion of the fructofuranose to the fructopyranose. The rate of this reversible reaction is the same as the rate for the mutarotation of levulose.[4] The two phenomena represent different directions of the same reversible reaction and the mutarotation of levulose consists in the partial conversion of a fructopyranose to a fructofuranose. This conclusion leads to some very interesting and important deductions which are discussed in the following sections.

[4] The equality of the mutarotations of levulose and of the fructose set free from sucrose by invertase is confirmed by our calculations of velocity constants as set forth on page 792 of this paper.

V. CHARACTER OF THE COMPLEX MUTAROTATION REACTIONS

Our investigations of the mutarotation reactions have been inspired by the desire to ascertain what modifications of the sugars are present in aqueous solutions and how rapidly the modifications change from one form to another. This problem has been attacked by studying the products resulting from reactions taking place in solution under conditions where the interconversion of the various isomers is slow, and by investigating the rates and mechanisms of the reactions. These studies have revealed that the equilibrium solutions of certain sugars, as for example galactose, arabinose, and talose, contain products other than the normal alpha and beta sugars. The oxidation of mannose $CaCl_2.4H_2O$ led to the inference that these modifications of unknown structure are furanoses, but independent evidence was needed to support this idea. We believe that the correlation of the mutarotation of levulose with the rapid reactions characteristic of the complex mutarotations of certain aldoses, in conjunction with the mutarotation of the fructofuranose set free from sucrose, shows that the rapid mutarotation reactions, with "heats of activation of about 14,000" and characterized by relatively high heats of reaction and by exceptionally marked sensitivity to acid and basic catalysts, are pyranose-furanose interconversions and that the complex mutarotations arise, at least largely, from the establishment of an equilibrium between the furanoses and the normal alpha and beta pyranoses. Presumably the equilibrium involves small concentrations of the open-chain modifications, but on account of the low concentrations these do not materially affect the optical rotations. Further study of the mutarotation of levulose will provide additional information about the pyranose-furanose interconversions and should lead to intimate knowledge of the mechanisms of the reactions and the determination of the minor constituents.

VI. STRUCTURE AND MUTAROTATION OF LACTULOSE

Lactulose, or 4-galactosido-fructose, first prepared by Montgomery and Hudson [44], exhibits a mutarotation reaction which is similar to that of levulose but differs in that it takes place in the opposite direction. If the mutarotation of lactulose be the reverse of the mutarotation of levulose, it should consist in the partial conversion of a furanose to a pyranose. It is therefore of importance to ascertain whether the mutarotation of lactulose is like the mutarotation of levulose except for direction. The similarity of the mutarotations of levulose and lactulose is shown by the following experimental results: (1) The thermal mutarotations given in table 9 reveal that the equilibrium between the various modifications of the two sugars varies with temperature in the same manner. In both cases, lowering the temperature shifts the equilibrium towards the more levorotatory modification; (2) the heats of activation for the two reactions, 14,900 and 15,800, are comparable and differ from the heats of activation for alpha-beta pyranose interconversions; (3) the catalytic effects of acids and bases on the rates for the two reactions are very pronounced, even in slightly acid solutions, and (4) the minimum mutarotation rates, 0.055 and 0.043 at 20° C, are comparable. The changes in optical rotation as well as the changes in volume show that the two reac-

tions, if alike, take place in opposite directions. Thus it appears that the mutarotation of lactulose is analogous to that of levulose but differs in that the less levorotatory modification is the known crystalline product. Since the mutarotation of levulose presumably results from the conversion of the pyranose to the furanose, the mutarotation of lactulose presumably results from the partial conversion of the furanose to pyranose, and in all probability crystalline lactulose is a furanose sugar, namely, 4-galacto-pyranosido-fructofuranose.

VII. STRUCTURE AND MUTAROTATION OF 1,3,4-TRIMETHYL-FRUCTOFURANOSE

In 1931 Hibbert, Tipson, and Brauns [45] reported a crystalline sugar which they designated as 1,3,4-trimethyl-fructofuranose. Since the hydroxyls on carbons 5 and 6 are free, the methylated sugar might crystallize in either the furanose or pyranose modification. From a comparison of the properties of the 1,3,4-trimethyl-fructose with those of 3,4,6-trimethyl-fructose, Hibbert, Tipson, and Brauns concluded that the crystalline sugar was a furanose. This important conclusion receives confirmation by comparison of its mutarotation with the mutarotations of levulose and lactulose. As may be seen from the data of table 5 (taken from the publication of Hibbert, Tipson, and Brauns [45]), 1,3,4-trimethyl-fructofuranose exhibits mutarotation. The optical rotation changes from a less levorotatory to a more levorotatory value at a rate comparable to that of levulose. The mutarotation is analogous to that of lactulose and the reverse of that of levulose. Hence it seems probable that the less levorotatory form of 1,3,4-trimethyl-fructose is the furanose modification and that the crystalline sugar is properly classified as a furanose.

TABLE 5.—*Mutarotation of 1,3,4-trimethyl-fructose* [1]

Time	$[\alpha]_D^{21}$	$m \times 10^3$	Time	$[\alpha]_D^{21}$	$m \times 10^3$
Minutes			*Minutes*		
4	−23.8	------	30	−51.4	69.0
5	−26.5	43.9	60	−51.85	------
6	−29.2	46.4			
17	−40.7	30.8	Average		[2] 49.2
20	−48.3	56.1			

[1] Data of Hibbert, Tipson, and Brauns [45].
[2] The minimum mutarotation constant for levulose is 55×10^{-3}.

VIII. MUTAROTATIONS OF OTHER FRUCTOSE DERIVATIVES

The validity of the hypothesis that the mutarotation of levulose consists for the most part in a pyranose-furanose interconversion can be tested by the investigation of related sugars in which the formation of either the furanose or pyranose ring is prevented by substitution on the fifth or sixth carbon. Previously Hudson [46] observed that tetraacetyl fructose prepared by him and Brauns [47] does not exhibit mutarotation. The corresponding 1,3,4,5-tetramethyl-fructose was reported by Irvine and Patterson [48] to have a very small mutarotation in which the specific rotation changes from −124.3 to −123.2.

This change [5] is small in comparison with the large change found for the mutarotation of levulose. Probably the mutarotation is caused by a normal alpha-beta interconversion, in which connection it will be recalled that we have shown [49] that sorbose gives a complex mutarotation consisting in a small rapid change accompanied by a small slow change. The small slow change during the mutarotation of sorbose appears to be caused by an alpha-beta pyranose interconversion. This indicates that the alpha-beta interconversion occurs in the pyranose ketose series but that the equilibrium lies far to one side, so that the establishment of equilibrium results in the formation of only small quantities of the beta pyranoses. Unfortunately we did not have 1,3,4,5-tetramethyl-fructose and therefore the determination of the effect of temperature on the mutarotation reaction and the study of other properties which might be used to ascertain whether it gives a rapid mutarotation reaction must remain for future investigation.

TABLE 6.—*Thermal mutarotation of 3,4,6-trimethyl-fructose* [1]

Time	Saccharimeter reading	$m \times 10^3$	Time	Saccharimeter reading	$m \times 10^3$
Minutes	°S		*Minutes*	°S	
0	(7.82)	------	60.77	8.73	7.4
6.23	8.53	------	76.70	8.75	6.8
9.55	8.55	8.2	90.36	8.77	------
14.63	8.57	6.7	150.73	8.81	------
19.55	8.59	6.5	Equilibrium	8.86	------
30.30	8.66	9.0			
47.39	8.70	7.6	Average	----------	7.5

[1] Change observed after cooling a 2.5-percent aqueous solution from 26 to 0.2° C.

This sample was furnished us by the courtesy of R. F. Jackson and Emma McDonald, of this Bureau.

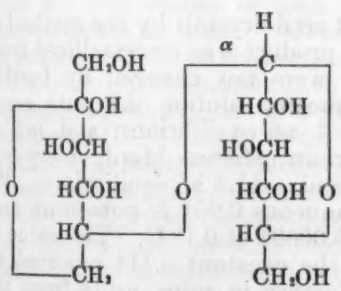
The study of another sugar which cannot form the pyranose ring was expedited by R. F. Jackson and Emma McDonald, of this Bureau, who very kindly provided us with a small quantity of 3,4,6-trimethyl-fructose. Although this sugar is known only in the form of a sirup, the absence, or existence, of the characteristic levulose mutarotation reaction can be ascertained by studying the change in optical rotation which follows a change in temperature. It will be recalled that when a solution of levulose is cooled a mutarotation takes place, which shows that lowering the temperature shifts the equilibrium towards the more levorotatory modification. It is evident a priori that if the same reaction occurs for trimethyl-fructose as occurs for levulose, the mutarotation which follows a decrease in temperature should reveal a change corresponding to the formation of the more levorotatory modification. It may be observed from the data for 3,4,6-trimethyl-fructose given in table 6 that lowering the temperature shifts the equilibrium towards a more dextrorotatory substance. This equilibrium shift is much smaller and in the opposite direction to that found for the thermal mutarotation of levulose and, since it is not probable that methylation would alter the relative energy content of two closely related stereoisomers the reaction does not appear to be the same as the reaction which predominates in the thermal mutarota-

[5] This mutarotation is to be investigated further because a somewhat larger mutarotation is reported to occur in benzene solution.

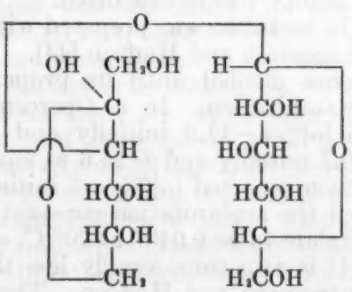
tion of levulose. It is noted, however, that the rate, 0.0075, for the thermal mutarotation of 3,4,6-trimethyl-fructose does not differ widely from the rate, 0.009, for the thermal mutarotation of levulose. The significance of this agreement, if it has any significance, is that the rate of the pyranose-furanose interconversion for levulose does not differ widely from the rate of a reaction which may consist in the interconversion of the alpha and beta furanose modifications of 3,4,6-trimethyl-fructose. The preparation and study of other sugars which cannot form both the pyranose and furanose rings is in progress and will be reported in future publications.

IX. MUTAROTATION AND STRUCTURE OF TURANOSE

The structure of turanose represented by formula I was assigned by Pacsu [50] in 1931, but as he points out in a recent paper [51], this structure does not account for the five octa-acetates which have been prepared. If structure I were correct, turanose would not exhibit a pyranose-furanose mutarotation because the hydroxyl on the fifth carbon would be blocked. The mutarotation of turanose, including the effect of temperature changes on the equilibrium state and on the reaction rates, is like the mutarotation of levulose and like other mutarotations which we have shown to consist in the interconversion of the pyranose and furanose modifications. This is evidence that the hydroxyl groups on both the fifth and sixth carbons in the fructose portion of the turanose molecule are free. Since turanose forms an osazone, the hydroxyl on the first carbon is also free. Hence the glucosidic group must be attached on either carbon 3 or carbon 4. If the glucosidic group were attached to carbon 4, and if these sugars have like rings for the glucosidic group, the osazone of turanose would be identical with the osazone of either cellobiose or maltose. Although the osazones of maltose [52], cellobiose [53], and turanose [54] are known products, they were prepared again in order to be certain that they are distinct substances. We found that the three substances have different optical rotations, melting points, and solubilities, and therefore they must be separate substances, and the glucosidic group of turanose cannot be combined with the fourth carbon. In all probability the structure of turanose corresponds to formula II.



I. Pacsu formula for turanose.



II. Proposed formula for turanose.

The conclusion that the ordinary mutarotation of levulose requires the existence of free hydroxyls on carbons 5 and 6 also explains the lack of appreciable mutarotation of hepta-acetyl turanose [55] without the

postulation of an orthoacid structure. This compound is analogous to tetra-acetyl-fructose and appears to be different from the orthoacids which contain a free hydroxyl. As we have shown previously [20], the latter compounds are very sensitive towards weak alkali, pyridine, and methyl alcohol, whereas hepta-acetyl-turanose was prepared by using silver carbonate and was recrystallized from alcohol without decomposition. Judging from its stability in alcoholic solution, it is probable that hepta-acetyl-turanose is a normal acetate rather than an orthoacid.

X. EXPERIMENTAL PROCEDURE

1. PREPARATION AND PURIFICATION OF THE SUGARS

The sugars used in this investigation were carefully purified and finally recrystallized slowly from water or aqueous alcohol. The *α-d*-galactose and *β-d*-galactose were part of the supply used for the measurements previously reported [2].

The sample of levulose was obtained by several recrystallizations of a sample of pure, white, crystalline levulose originally prepared in the Bureau's levulose plant. The final recrystallization of the levulose sample was made from aqueous alcohol, while the massecuite was kept in motion. In a 4-percent aqueous solution the sugar gave $[\alpha]_D^{20} = -132.2$ initially and -92.4 at equilibrium; and $[\alpha]_D^0 = -132.9$ initially and -103.4 at equilibrium. The mutarotation constants in the presence of 0.005 *N* potassium acid phthalate buffer (pH=4.6) were found to be 0.0592 at 20.05° C and 0.0090 at 0° C.

The turanose was prepared from melezitose by the method of Hudson and Pacsu [56]. Crystallization was induced by seed furnished by D. H. Brauns from his original sample. The product so obtained, after recrystallization from aqueous alcohol, gave in a 4-percent aqueous solution $[\alpha]_D^{20.7} = +27.3$ initially and $+75.8$ at equilibrium; and $[\alpha]_D^{0.2} = +27.8$ initially and $+70.0$ at equilibrium; whereas Hudson and Pacsu reported an initial value of $+22$ at 22° C and an equilibrium value of $+75.3$. We found the mutarotation constant to be 0.086 at 20.7° C, and 0.0136 at 0.2° C, in a solution of 0.005 *N* potassium acid phthalate buffer (pH=4.6); whereas Hudson and Pacsu found a constant of 0.097 in an aqueous solution for which the acidity was not reported.

The lactulose was prepared without seed crystals by the method of Montgomery and Hudson [44]. The product was recrystallized from aqueous alcohol until its properties were not changed by further recrystallization. In a 4-percent aqueous solution the pure sugar gave $[\alpha]_D^{20} = -11.9$ initially and -50.7 at equilibrium; and $[\alpha]_D^{0.1} = -10.7$ initially and -56.6 at equilibrium; whereas Montgomery and Hudson reported $[\alpha]_D^{22} = -5$ initially and -51.5 at equilibrium. We found the mutarotation constant in aqueous 0.001 *N* potassium acid phthalate to be 0.0435 at 20° C, and 0.00604 at 0.1° C. The value at 20° C is also considerably less than the constant 0.114 reported by Montgomery and Hudson. The difference in rates, aside from the small difference in temperature, may be due to a difference in acidity, which varies with the carbon dioxide content of the water used in making the measurements.

2. MUTAROTATION MEASUREMENTS

The sample was placed in a dry 100-ml glass-stoppered flask and 50 ml of water or the buffered solution at the desired temperature was added quickly with agitation. Time was measured with a stop watch, starting with the addition of the water. The optical rotations were measured in a 4-dm Schmidt & Haensch water-jacketed tube on a Bates saccharimeter. The conversion factor 0.3462 was used throughout for converting degrees sugar to angular degrees. The readings in degrees sugar are converted to specific rotations by multiplying by the ratio of the equilibrium specific rotation to the observed equilibrium rotation in sugar degrees.

A summary of the mutarotation constants obtained from measurements in solutions containing acids and bases is given in table 3, page 779; in table 7 the measurements on the ketoses are summarized; while the experimental data for a part of the measurements are given in table 11.

The method for calculating the velocity constants is described in detail on page 156 of reference [2]. Briefly, the values of m_1 are calculated from the equation

$$m_1=\frac{1}{t_2-t_1}\log\frac{r_1-r_\infty}{r_2-r_\infty} \tag{3}$$

using values for t_1, t_2, r_1, and r_2, obtained after the virtual completion of the fast reaction. The values of m_2 for the rapid reactions are calculated from the equation

$$m_2=\frac{1}{t_2-t_1}\log\frac{d_1}{d_2} \tag{4}$$

in which d_1 and d_2 represent the differences between the observed rotations at various times and those obtained by extrapolation of the long period back to the same time. For levulose, lactulose, and turanose, however, the slow reaction is absent or negligibly small, and therefore the values for m_2 are calculated from the usual mutarotation equation. All velocity constants are given in common logarithms.

The buffered solutions were prepared from ordinary distilled water, saturated with carbon dioxide air, by adding the reagents indicated in table 8. The acidity of each solution was determined by using a glass-electrode pH meter. Measurements of pH were made before adding the sugar and after the mutarotation was complete. Since the anions of the acids used as buffers have marked catalytic effects, the velocity constants for the sugars in buffered solutions are larger than those which would be obtained in the absence of these buffers. Our results indicate that *o*-nitrophenol has a relatively small catalytic effect and consequently the catalytic coefficients for the hydroxyl ion were calculated from the measurements in which this buffer was used. The equations thus obtained are empirical and only approximate the results obtained from measurements at points of intermediate acidity. Probably the differences are due to the catalytic action of the various buffers.

Even though we had measured the mutarotation of α-*d*- and β-*d*-galactose previously, new measurements were made in buffered solutions because our experience with levulose indicated that in non-buffered solutions differences in acidity frequently cause variations in the constants which are far greater than the errors of the observations. In the buffered solutions like values for m_1 and for m_2 were obtained

from alpha and beta galactose. The agreement of the constants as obtained from the two sugars is far too close to be merely a matter of chance and therefore it is pertinent to the interpretation of the reactions.

The mutarotation measurements with levulose $CaCl_2.3H_2O$ reported in table 11 were made in order to ascertain whether previous investigators [57] might have overlooked a rapid initial mutarotation. The mutarotation was found to be like the mutarotation of levulose and hence the sugar constituent of levulose $CaCl_2.3H_2O$ is the normal form of levulose.

TABLE 7.—*Summary of optical rotatory measurements for ketose sugars*

Concentration	Temperature	Initial	Equilibrium	Molecular rotation	Solvent for mutarotation	pH at 20° C	$[\alpha]_D$ "t" minutes after sugar is dissolved	Ref.
				LEVULOSE				
g/100 ml	°C	$[\alpha]_D$	$[\alpha]_D$	$[M]$				
4.0	20.05	−132.2	−92.4	−23,810	0.005 *N* KH phthalate buffer 2.	4.6	$-39.8\times10^{-.0093t}-92.4$	[30]
4.0	20.00				0.001 *N* KH phthalate buffer 6.	4.4	$-39.8\times10^{-.0161t}-92.4$	[30]
3.9	0.00	−132.9	−103.4	−23,930	0.005 *N* KH phthalate buffer 2.	4.6	$-29.5\times10^{-.00903t}-103.4$	[31]
				TURANOSE				
4.1	20.70	+27.3	+75.8	+9,340	0.005 *N* KH phthalate buffer 2.	4.6	$-48.5\times10^{-.0081t}+75.8$	[56]
3.9	0.20	+27.8	+70.0	+9,510	do	4.6	$-42.2\times10^{-.0138t}+70.0$	[56]
				LACTULOSE				
3.9	20.00	−11.9	−50.7	−4,070	0.001 *N* KH phthalate buffer 6.	4.4	$+38.8\times10^{-.0433t}-50.7$	[44]
3.8	0.10	−10.7	−56.6	−3,660	do	4.4	$+45.9\times10^{-.0056t}-56.6$	[44]
				l-SORBOSE [1]				
11.3	20.0	−44.3	−43.4	−7,980	Distilled water		$-0.86\times10^{-.0424t}+0.59\times10^{-.331t}-43.4$	[49]
11.6	0.4	−43.9	−43.3	−7,910	do		$-0.55\times10^{-.0084t}+0.30\times10^{-.0891t}-43.3$	[49]

[1] The measurements for *l*-sorbose were reported in a previous publication [49].

TABLE 8.—*Compositions of the buffered solutions*

Buffer	Method of preparation	pH at 20° C	Total molarity of buffer
KH phthalate buffer 1	6.0 ml of 0.1007 *N* HCl was added to 50 ml of 0.1000 *N* KH phthalate and solution diluted to 1 liter.	4.0	0.005
KH phthalate buffer 2	8.0 ml of 0.1064 *N* NaOH was added to 50 ml of 0.1000 *N* KH phthalate and solution diluted to 1 liter.	4.6	.005
KH phthalate buffer 3	34.6 ml of 0.1064 *N* NaOH was added to 500 ml of 0.0100 *N* KH phthalate and solution diluted to 1 liter.	5.6	.005
KH phthalate buffer 4	40.0 ml of 0.1064 *N* NaOH was added to 500 ml of 0.0100 *N* KH phthalate and solution diluted to 1 liter.	6.1	.005
KH phthalate buffer 5	45.4 ml of 0.1064 *N* NaOH was added to 500 ml of 0.0100 *N* KH phthalate and solution diluted to 1 liter.	6.45	.005
KH phthalate buffer 6	0.204 g of KH phthalate was dissolved in 1 liter	4.4	.001
o-Nitrophenol buffer 1	12.0 ml of 0.1064 *N* NaOH was added to 1 liter of solution saturated [1] at 20° C.	6.4	.01
o-Nitrophenol buffer 2	30.0 ml of 0.1064 *N* NaOH was added to 1 liter of solution saturated [1] at 20° C.	6.9	.01
Succinic acid buffer 1	315 ml of 0.1064 *N* NaOH was added to 1 liter of 0.1000 *M* succinic acid solution.	3.8	.08
Succinic acid buffer 2	0.118 g of succinic acid dissolved in 1 liter	3.7	.001

[1] This approximately saturated solution contains 1.50 g of *o*-nitrophenol per liter of solution. The total molarity of the *o*-nitrophenol in the buffer solutions is approximately 0.01 *M*. The greater solubility of *p*-nitrophenol may make *p*-nitrophenol preferable for the preparation of buffer solutions in the range pH=6 to 8.5.

3. THERMAL MUTAROTATIONS

An 8- to 10-percent sugar solution in a 4-dm water-jacketed silver tube was allowed to reach equilibrium at the upper temperature (25 to 30° C) and its optical rotation was then read. The water was drained from the jacket and a mixture of water and alcohol cooled to 0° C was pumped through the jacket. Time was measured from the moment when the cold circulating liquid was turned on. When the temperature became constant (about 5 minutes after cooling started) at approximately 0° C, saccharimeter readings were made and the velocity constants calculated in the usual manner. The thermal mutarotation of 3,4,6-trimethyl-fructose is reported on page 786, while the thermal mutarotation of *d*-galactose is reported on page 190 of reference [2]. The thermal mutarotations of levulose, lactulose, and turanose are reported in table 9.

TABLE 9.—*Thermal mutarotations of levulose, lactulose, and turanose*

Time	Saccharimeter reading	$m \times 10^3$	Time	Saccharimeter reading	$m \times 10^3$
Levulose [1] at 0.10° C					
Minutes	°S		*Minutes*	°S	
0	(−82.69)		50.30	−92.32	9.11
6.35	−86.20		59.94	−93.04	9.07
10.17	−86.98	9.08	75.36	−93.93	9.00
15.06	−87.94	9.37	90.83	−94.58	8.95
20.06	−88.79	9.32	134.56	−95.62	8.87
25.00	−89.54	9.28	24 hr	−96.36	
30.23	−90.26	9.28			
39.88	−91.36	9.18	Average		9.14
Lactulose [2] at 0.15° C					
0	(−55.84)		50.62	−61.24	6.71
7.94	−56.62		60.80	−61.93	6.65
12.10	−57.18	6.30	75.43	−62.73	6.55
16.60	−57.82	6.72	91.41	−63.43	6.47
20.58	−58.33	6.76	120.20	−64.32	6.32
25.12	−58.87	6.77	167.38	−65.18	6.13
32.19	−59.64	6.79	20 hr	−66.19	
39.92	−60.39	6.80			
			Average		6.58
Turanose [3] at 0.15° C					
0	(89.96)		30.70	+83.97	12.5
6.38	+87.23		40.72	+83.16	12.5
7.70	+86.97	13.4	50.98	+82.56	12.4
9.95	+86.59	12.6	72.08	+81.74	12.3
15.12	+85.76	12.7	90.50	+81.35	12.2
19.92	+85.15	12.4	22 hr	+80.74	
25.43	+84.52	12.3			
			Average		12.5

[1] Change observed after cooling an 8-percent aqueous solution buffered with 0.001 *N* potassium acid phthalate from 25 to 0.10° C. The reading at zero time was made at 25° C.

[2] Change observed after cooling a 10-percent solution buffered with 0.001 *N* potassium acid phthalate from 27 to 0.15° C.

[3] Change observed after cooling a 10-percent aqueous solution buffered with 0.001 *N* potassium acid phthalate at pH 4.4 from 26 to 0.15° C.

4. MUTAROTATION AFTER INVERSION OF SUCROSE

The method developed for analyzing the complex mutarotations is especially useful for studying the mutarotations which follow the splitting of sugars by enzymes. Thus when sucrose is split by invertase the mutarotation of the glucose set free can be considered to represent the slow reaction, m_1, while the mutarotation of the fructofuranose can be considered to represent the fast reaction, m_2. The value of m_1 is obtained from the observed rotations after the rapid reaction is complete by application of the usual formula, and the value of m_2 is obtained from the equation

$$m_2=\frac{1}{t_2-t_1}\log\frac{d_1}{d_2},$$

where d_1 and d_2 represent the differences between the extrapolated slow mutarotation and the observed rotations. As may be observed from the results reported in table 10, application of these equations to the data of Purves and Hudson [58] gives very satisfactory values for the mutarotation constants of the glucose and fructose constituents. The velocity constant for the mutarotation of the fructose component (0.0530) at pH 4.5 buffered with sodium acetate is in agreement with that (0.0548) which we obtained for the reverse reaction in a solution at pH 4.4 buffered with potassium acid phthalate and at the same temperature. The constant for α-*d*-glucose (0.00632) is also in excellent agreement with that (0.00648) found for the mutarotation of the freshly dissolved α-*d*-glucose in aqueous solution at pH 4.6.

TABLE 10.—*Mutarotation of fructofuranose and α-d-glucose liberated from sucrose by invertase* [a]

Fructose constituent				Glucose constituent		
Time	Purves and Hudson reading	Deviation	$m_2\times10^3$	Time	Purves and Hudson reading	$m_1\times10^3$
Minutes	°V	°V		*Minutes*	°V	
3.3 [b]	19.95	16.21	----	30.0	−0.81	----
4.1	18.36	14.80	(49.4)	35.0	−1.79	----
5.0	16.63	13.27	51.1	40.0	−2.64	----
6.2	14.68	11.57	50.5	50.0	−3.94	6.64
7.0	13.41	10.48	51.2	60.3	−4.99	6.33
8.0	12.01	9.29	51.4	80.5	−6.69	6.25
9.1	10.46	7.96	53.3	190.0	−10.57	5.79
10.0	9.33	7.02	54.2	29 hr	−11.81	----
11.0	8.43	6.32	53.1			
12.0	7.41	5.50	54.0	Average	----	6.25
13.0	6.46	4.75	55.0			
15.1	4.96	3.65	54.9			
17.0	3.86	2.90	54.6			
Average	----	----	53.0			

[a] Calculations based on data taken from the paper of Purves and Hudson, J. Am. Chem. Soc. 56, 706 (1934). The temperature was 20° C and the pH was 4.5.

[b] Although Purves and Hudson give earlier data, the calculations were begun at 3.3 minutes, at which time we considered the inversion to be practically complete. The slow reaction is calculated from the reading at 40 minutes.

XI. EXPERIMENTAL DATA FOR MUTAROTATION MEASUREMENTS

The experimental data for the mutarotation measurements conducted in buffered solutions at approximately pH 4.6 are recorded in table 11. These measurements are representative of those used for determining the constants given in table 3. In order to conserve space the optical-rotation measurements at other acidities are not given in detail.

TABLE 11.—*Experimental data for the mutarotation measurements in buffered solutions*

LEVULOSE

3.9 g per 100 ml at 0.00° C Read in a 4-dm tube (pH=4.61 at 20° C) KH phthalate buffer 2			4.0 g per 100 ml at 20.05° C Read in a 4-dm tube (pH=4.57 at 20° C) KH phthalate buffer 2		
Time	Observed reading	$m\times10^3$	Time	Observed reading	$m\times10^3$
Minutes	°S		*Minutes*	°S	
2.39	−59.22		1.45	−57.81	
4.10	−58.81	(8.38)	2.52	−55.71	60.7
10.10	−57.32	9.18	4.49	−52.65	59.7
21.46	−55.04	9.15	7.61	−49.24	59.0
30.53	−53.60	9.09	9.93	−47.47	59.0
40.39	−52.29	9.09	12.96	−45.87	58.9
50.02	−51.27	9.05	15.99	−44.81	58.8
60.45	−50.37	9.02	19.87	−43.96	58.6
76.73	−49.34	8.91	170	−42.70	
89.80	−48.70	8.89			
105.57	−48.11	8.91	Average		59.2
22hr	−46.59				
Average		9.03			

LEVULOSE $CaCl_2.3H_2O$

7.9 g per ml at 20.55° C Read in a 4-dm tube (pH=3.88 at 20° C) KH phthalate buffer 2					
Time	Observed reading	$m\times10^3$	Time	Observed reading	$m\times10^3$
Minutes	°S		*Minutes*	°S	
2.10	−74.01		10.60	−61.50	67.6
2.91	−72.17	(61.2)	12.76	−60.17	68.0
3.69	−70.43	64.4	15.96	−58.91	67.9
4.59	−68.63	66.1	19 hr	−56.96	
5.41	−67.23	66.5			
6.75	−65.28	67.0	Average		66.9
8.71	−63.08	67.3			

TABLE 11.—*Experimental data for the mutarotation measurements in buffered solutions*—Continued

LACTULOSE

3.8 g per 100 ml at 0.1° C Read in a 4-dm tube (pH=4.42 at 20° C) 0.001 *N* KH phthalate solution 6			3.9 g per 100 ml at 20.0° C Read in a 4-dm tube (pH=4.40 at 20° C) 0.001 *N* KH phthalate solution 6		
Time	Observed reading	$m \times 10^3$	Time	Observed reading	$m \times 10^3$
Minutes	°S		*Minutes*	°S	
2.36	−5.35		1.56	−7.95	
3.19	−5.59	(6.49)	2.41	−9.19	(44.1)
5.64	−6.22	6.05	3.77	−10.88	42.7
11.31	−7.66	6.13	4.98	−12.27	43.1
19.88	−9.60	6.11	7.69	−14.84	43.6
30.12	−11.63	6.10	9.47	−16.14	43.4
39.97	−13.30	6.06	12.12	−17.74	43.5
49.73	−14.75	6.05	14.95	−19.07	43.9
60.06	−16.10	6.05	17.6	−20.03	44.1
74.86	−17.70	6.03	22.05	−21.05	43.8
90.05	−19.03	6.01	19 hr	−22.95	
105.33	−20.12	6.00	Average		43.5
122.33	−21.09	5.99			
174.08	−22.96	5.95			
23 hr	−24.81				
Average		6.04			

TURANOSE

3.9 g per 100 ml at 0.2° C Read in a 4-dm tube (pH=4.61 at 20° C) KH phthalate buffer 2			4.1 g per 100 ml at 20.70° C Read in a 4-m tube (pH=4.61 at 20° C) KH phthalate buffer 2		
Time	Observed reading	$m \times 10^3$	Time	Observed reading	$m \times 10^3$
Minutes	°S		*Minutes*	°S	
4.03	+14.80		1.65	+19.13	
5.08	+15.39	(14.8)	3.29	+23.69	86.2
10.25	+17.83	13.9	4.67	+26.54	86.4
14.95	+19.70	13.7	6.45	+29.21	86.2
20.90	+21.69	13.6	8.60	+31.42	86.4
26.62	+23.30	13.5	11.47	+33.20	86.1
33.80	+24.96	13.5	14.39	+34.19	85.1
40.58	+26.24	13.5	19.20	+35.00	(84.5)
50.35	+27.63	13.5	20 hr	+35.54	
60.65	+28.73	13.5	Average		86.1
75.02	+29.76	13.5			
90.33	+30.46	13.5			
19 hr	+31.62				
Average		13.6			

TABLE 11.—*Experimental data for the mutarotation measurements in buffered solutions*—Continued

α-d-GLUCOSE

3.9 g per 100 ml at 0.10° C Read in a 4-dm tube (pH=4.61 at 20° C) KH phthalate buffer 2			3.9 g per 100 ml at 20.05° C Read in a 4-dm tube (pH=4.60 at 20° C) KH phthalate buffer 2		
Time	Observed reading	$m_1 \times 10^3$	Time	Observed reading	$m_1 \times 10^3$
Minutes	°S	(k_1+k_2)	*Minutes*	°S	(k_1+k_2)
2.82	+49.75		1.55	+49.84	
5.02	+49.65	0.764	10.07	+46.72	6.56
9.93	+49.41	.806	20.09	+43.56	6.52
16.45	+49.10	.809	29.97	+40.91	6.48
22.08	+48.85	.796	45.25	+37.47	6.47
30.17	+48.52	.771	59.95	+34.84	6.46
44.95	+47.90	.762	75.32	+32.61	6.47
60.13	+47.30	.752	90.21	+30.91	6.46
94.68	+45.95	.749	121.20	+28.38	6.44
116.77	+45.13	.747	18 hr	+24.00	
178.95	+42.94	.751	Average		6.48
227.17	+41.44	.747			
270.92	+40.13	.750			
362.00	+37.76	.750			
48 hr	+23.80				
Average		0.766			

α-d-GALACTOSE

3.9 g per 100 ml at 0.15 to 0.30° C Read in a 4-dm tube (pH=4.62 at 20° C) KH phthalate buffer 2					4.0 g per 100 ml at 20.05° C Read in a 4-dm tube (pH=4.55 at 20° C) KH phthalate buffer 2				
Time	Observed reading	$m_1 \times 10^3$	Deviation	$m_2 \times 10^3$	Time	Observed reading	$m_1 \times 10^3$	Deviation	$m_2 \times 10^3$
Minutes	°S		°S		*Minutes*	°S		°S	
3.62	+68.91		1.31		2.10	+66.52		1.84	
9.58	+68.33		1.11	12.1	3.10	+65.72		1.58	(66.2)
15.21	+67.83		0.98	10.9	4.98	+64.20		1.11	76.2
21.66	+67.26		.82	11.3	7.37	+62.76		0.76	72.9
32.87	+66.37		.63	10.9	9.93	+61.28		.50	72.3
42.28	+65.60		.43	12.5	12.08	+60.18		.37	69.8
51.91	+64.96		.36	11.6	14.14	+59.14		.22	76.6
60.91	+64.29		.21	13.9	30.20	+53.05			
118.30	+60.96				39.94	+50.28	8.22		
147.47	+59.55	0.953			49.93	+47.91	8.25		
205.30	+56.93	.973			60.08	+45.93	8.24		
255.21	+54.92	.979			75.08	+43.60	8.27		
316.84	+52.81	.970			89.97	+41.88	8.26		
359.77	+51.47	.971			121.43	+39.51	8.25		
394.81	+50.49	.968			150.09	+38.26	8.31		
48 hr	+38.21				19 hr	+36.60			
Average		0.969		11.9	Average		8.26		73.6

TABLE 11.—*Experimental data for the mutarotation measurements in buffered solutions*—Continued

β-d-GALACTOSE

3.7 g per 100 ml at 0.20° C Read in a 4-dm tube (pH=4.61 at 20° C) KH phthalate buffer 2					4.0 g per 100 ml at 20.50° C Read in a 4-dm tube (pH=4.67 at 20° C$_1$) KH phthalate buffer 2				
Time	Observed reading	$m_1 \times 10^3$	Deviation	$m_2 \times 10^3$	Time	Observed reading	$m_1 \times 10^3$	Deviation	$m_2 \times 10^3$
Minutes	°S		°S		*Minutes*	°S		°S	
2.27	+23.95		0.89		1.43	+24.38		1.68	
9.53	+24.01		.75	10.2	2.47	+24.35		1.37	(85.2)
14.88	+24.05		.65	10.8	3.19	+24.39		1.22	78.9
20.89	+24.07		.52	12.5	3.95	+24.43		1.06	79.4
30.17	+24.20		.41	12.1	4.77	+24.49		0.91	79.7
41.05	+24.34		.27	13.4	6.12	+24.65		.73	77.2
50.02	+24.49		.20	13.6	8.34	+24.96		.50	76.2
61.41	+24.70		(.13)	(14.1)	10.31	+25.25		.33	79.6
120.52	+25.90				12.67	+25.67		.22	78.5
154.25	+26.60	0.918			30.03	+28.67			
179.77	+27.09	.912			39.97	+30.05	8.33		
212.91	+27.66	.893			49.98	+31.23	8.46		
259.32	+28.43	.895			60.20	+32.22	8.52		
319.15	+29.35	.906			75.09	+33.35	8.56		
48 hr	+36.07				90.02	+34.17	8.52		
					124.78	+35.39	8.55		
Average		0.905		12.1	155.91	+35.97	8.64		
					19 hr	+36.62			
					Average		8.51		78.5

XII. GENERAL SUMMARY

The changes in optical rotation, molecular volume, molecular refraction, and energy content which occur after dissolving levulose and α-*d*-galactose in water clearly show that the mutarotation of levulose is caused by the same kind of reaction as causes the rapid mutarotation of α-*d*-galactose. The similarity of the two reactions and their resemblance to the rapid mutarotation reactions of other sugars are confirmed by the following observations: (1) Alterations in temperature cause large changes in the equilibrium proportions of the labile substances responsible for both the mutarotation of levulose and for the rapid mutarotation reactions; (2) the heat of activation for the reaction representing the mutarotation of levulose is comparable with the heat of activation for the rapid mutarotation reactions, and (3) the constants for the mutarotations of levulose and the rapid mutarotation reactions are both extremely sensitive to the catalytic action of acids and bases and vary with pH in like manner.

Attention is directed to the observation of Hudson that the mutarotation of the fructose liberated from sucrose by invertase occurs at the same rate as the mutarotation of levulose, but in the opposite direction. Since the fructose constituent of sucrose is a furanose and levulose is a pyranose, the mutarotation of fructose set free by invertase must be caused by the conversion of part of the freshly liberated fructofuranose to levulose. The mutarotation of levulose, which is the reverse, must be caused by the conversion of part of the freshly dissolved sugar to the fructofuranose. This conclusion leads to the following deductions: (1) That the mutarotation of lactulose is caused by a furanose-pyranose change and that cyrstalline lactulose is a furanose; (2) that the mutarotation of Hibbert's 1, 3, 4-trimethyl-

fructofuranose results from a furanose-pyranose change and that the sugar is properly classified as a furanose; (3) that the mutarotation of turanose results from a pyranose-furanose change and therefore the glucosidic group is not united with the fifth or sixth carbon but in all probability it is united with the third carbon; and (4) that the rapid reactions characteristic of the complex mutarotations of galactose and other sugars are pyranose-furanose interconversions, and the complex mutarotations arise from the establishment of an equilibrium between the furanoses and the normal α- and β-pyranoses.

The changes which occur during the thermal mutarotation of levulose, lactulose, and turanose are alike for the three sugars and correspond to the changes found in the equilibrium proportions of the labile constituent of galactose under like conditions. The application of "thermal mutarotations" for investigating the mutarotation reactions of sugars which are available only as sirups is illustrated by a study of the "thermal mutarotation" of 2,3,6-trimethyl-fructose.

Velocity constants determined in buffered solutions covering the range between pH 1 to 7 are reported for the mutarotations of glucose, galactose, and levulose. For the rapid reactions, the catalytic effects of hydrogen and hydroxyl ions are much greater than those found for the normal alpha-beta pyranose interconversions. The high sensitivity of the rapid mutarotation reactions to variations in acidity accounts for some of the discrepancies in the mutarotation constants obtained by using distilled water containing variable quantities of carbon dioxide. Hence for accurate measurements the acidity must be controlled. The mutarotation constants found for α-*d*-galactose and β-*d*-galactose in buffered solutions were the same within the experimental error. For lactulose, the mutarotation constant in 0.001 *N* potassium acid phthalate at pH 4 4 at 20° C was found to be 0.0435 with $[\alpha]_D^{20} = -11.9$ initially, and -50.7 at equilibrium; at 0.1° C the mutarotation constant was found to be 0.00604 with $[\alpha]_D^{0.1} = -10.7$ initially and -56.6 at equilibrium. For turanose, the mutarotation constant in a 4-percent aqueous solution buffered at pH 4.6 with 0.005 *N* potassium acid phthalate buffer at 20.7° C was found to be 0.086 with $[\alpha]_D^{20.7} = +27.3$ initially, and $+75.8$ at equilibrium; at 0.2° C the mutarotation constant was found to be 0.0136 with $[\alpha]_D^{0.2} = +27.8$ initially, and $+70.0$ at equilibrium. Mutarotation measurements with levulose in a 4-percent aqueous solution in the presence of 0.005 *N* potassium acid phthalate buffer at pH=4.6 gave $[\alpha]_D^{20} = -132.2$ initially, and -92.4 at equilibrium; and $[\alpha]_D^0 = -132.9$ initially, and -103.4 at equilibrium, with mutarotation constants of 0.0592 and 0.0090 at 20 and 0° C. The mutarotation of fructose $CaCl_2.3H_2O$ shows that this compound contains the normal modification of levulose.

XIII. REFERENCES

[1] H. S. Isbell and W. W. Pigman, BS J. Research **10,** 337 (1933) RP534.
[2] H. S. Isbell and W. W. Pigman, J. Research NBS **18,** 141 (1937) RP969.
[3] H. S. Isbell, J. Research NBS **18,** 505 (1937) RP990.
[4] L. J. Simon, Compt. rend. **132,** 487 (1901).
[5] H. S. Isbell, BS J. Research **3,** 1041 (1929) RP128.
[6] K. Freudenberg and R. Kuhn, Ber. deut. chem. Ges. **64,** 722 (1931).
[7] H. S. Isbell and C. S. Hudson, BS J. Research **8,** 327 (1932) RP418.
[8] H. S. Isbell, BS J. Research **8,** 615 (1932) RP441.
[9] C. N. Riiber and J. Minsaas, Ber. deut. chem. Ges. **60,** 2402 (1927).

[10] F. P. Phelps and F. J. Bates, J. Am. Chem. Soc. **56,** 1250 (1934).
[11] H. S. Isbell, BS J. Research **5,** 741 (1930) RP226.
[12] C. N. Riiber and O. Bjerkli, Kgl. Norske Videnskab Selskabs, Skrifter, No. 5 (1936).
[13] R. M. Hann, Alice T. Merrill, and C. S. Hudson, J. Am. Chem. Soc. **57,** 2100 (1935).
[14] C. S. Hudson and E. Yanovsky, J. Am. Chem. Soc. **39,** 1037 (1917).
[15] R. M. Hann and C. S. Hudson, J. Am. Chem. Soc. **59,** 550 (1937).
[16] H. S. Isbell, BS J. Research **5,** 1179 (1930) RP253; **7,** 1115 (1931) RP392.
[17] C. N. Riiber and J. Minsaas, Ber. deut. chem. Ges. **59,** 2266 (1926).
[18] G. F. Smith and T. M. Lowry, J. Chem. Soc. **1928,** 666.
[19] N. R. Sørensen, Kgl. Norske Videnskab Selskabs, Skrifter No. 2 (1937).
[20] W. W. Pigman and H. S. Isbell, J. Research NBS **19,** 189 (1937) RP1021.
[21] C. N. Riiber and N. A. Sørensen, Kgl. Norske Videnskab Selskabs, Skrifter, No. **7** (1933).
[22] E. M. Montgomery and C. S. Hudson, J. Am. Chem. Soc. **56,** 2074 (1934).
[23] F. P. Phelps, H. S. Isbell, and W. W. Pigman, J. Am. Chem. Soc. **56,** 747 (1934).
[24] J. K. Dale, BS J. Research **3,** 459 (1929) RP106.
[27] H. S. Isbell, J. Am. Chem. Soc. **56,** 2789 (1934).
[26] H. S. Isbell, J. Research NBS **20,** 97 (1938) RP1069.
[27] H. S. Isbell, J. Research NBS **19,** 639 (1937) RP1052.
[28] H. S. Isbell, J. Am. Chem. Soc. **55,** 2166 (1933).
[29] T. M. Lowry and G. F. Smith, Rapports sur les Hydrates de Carbone, 10th Conference of the International Union of Chemistry (Liége, p. 79, 1930).
[30] H. S. Isbell and W. W. Pigman, J. Research NBS **16,** 553 (1936) RP892.
[31] J. M. Nelson and F. M. Beegle, J. Am. Chem. Soc. **41,** 559 (1919).
[32] C. S. Hudson, J. Am. Chem. Soc. **30,** 1564 (1908).
[33] C. N. Riiber and V. Esp, Ber. deut. chem. Ges. **58,** 737 (1925).
[34] H. W. Wiley, J. Am. Chem. Soc. **18,** 81 (1896).
[35] C. S. Hudson, J. Am. Chem. Soc. **31,** 66 (1909).
[36] C. N. Riiber and N. A. Sørensen, Norges Tekniske Høiskole, Avhandlinger Til 25 Ars Jubileet (1935).
[37] C. S. Hudson, J. Am. Chem. Soc. **29,** 1571 (1907).
[38] R. Kuhn and P. Jacob, Z. physikal. Chem. **113,** 389 (1924).
[39] J. N. Brönsted and E. A. Guggenheim, J. Am. Chem. Soc. **49,** 2554 (1927).
[40] H. Euler and A. Hedelius, Biochem. Z. **107,** 150 (1920).
[41] C. S. Hudson, J. Am. Chem. Soc. **31,** 655 (1909).
[42] C. S. Hudson, J. Am. Chem. Soc. **52,** 1716 (1930).
[43] W. N. Haworth, The Constitution of Sugars p. 68 (Edward Arnold & Co., London, 1929).
[44] Edna M. Montgomery and C. S. Hudson, J. Am. Chem. Soc. **52,** 2101 (1930).
[45] H. Hibbert, R. S. Tipson, and F. Brauns, Canadian J. Research **4,** 235 (1931).
[46] C. S. Hudson, Sci. Pap. BS **21,** 365 (1926) S533.
[47] C. S. Hudson and D. H. Brauns, J. Am. Chem. Soc. **37,** 2736 (1915).
[48] J. C. Irvine and J. Patterson, J. Chem. Soc. London **121,** 2696 (1922); see also C. Anderson, W. Charlton, W. Haworth, and V. Nicholson, J. Chem. Soc. 1337 (1929).
[49] W. W. Pigman and H. S. Isbell, J. Research NBS **19,** 443 (1937) RP1035.
[50] E. Pacsu, J. Am. Chem. Soc. **53,** 3099 (1931).
[51] E. Pacsu and F. B. Cramer, J. Am. Chem. Soc. **59,** 1061 (1937).
[52] E. Fischer, Ber. deut. chem. Ges. **17,** 583 (1884).
[53] G. Zemplen, Z. Csuros, and Z. Bruckner, Ber. deut. chem. Ges. **61,** 927 (1928).
[54] E. Fischer, Ber. deut. chem. Ges. **27,** 2488 (1894).
[55] E. Pacsu, J. Am. Chem. Soc. **55,** 2451 (1933).
[56] C. S. Hudson and E. Pacsu, J. Am. Chem. Soc. **52,** 2519 (1930).
[57] A. B. Smith and B. Tollens, Ber. deut. chem. Ges. **33,** 1277 (1900).
[58] C. B. Purves and C. S. Hudson, J. Am. Chem. Soc. **56,** 706 (1934).
[59] R. F. Jackson and J. A. Mathews, BS J. Research **8,** 403 (1932) RP426.

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SUPERCOOLING AND FREEZING OF WATER

By N. Ernest Dorsey

ABSTRACT

This is a strictly preliminary report, rendered necessary by a temporary suspension of the work. No doubt attaches to the observations reported, but the setting of limits within which they are valid, and the determining of the most satisfactory way in which to explain them, should await further work. Contrary to current opinions, it has been found that the extreme supercooling of water (at least down to −21° C) is not dependent upon either extreme quiescence or upon the use of a minute volume, and that motes in the water exert a strong nonspecific effect. For each specimen there is a definite temperature (the spontaneous-freezing-point), characteristic of the specimen, at which ice suddenly appears, at which the water freezes spontaneously. The well-known fact that a preheating of the water may facilitate its supercooling has been found to depend upon a lasting change so produced in the water—a change that persists at room temperatures for at least 6 months, and that seems to be permanent. By sedimentation, the spontaneous-freezing-points of the extreme layers of a column of water become different, that of the bottom ones becoming higher than that of the top ones. All the observations are consistent with the idea that the spontaneous-freezing-point of a specimen is determined, within undetermined limits, by the size of the largest mote that it contains; the smaller the mote, the lower the spontaneous-freezing-point. The effect of agitation has been considered, and three distinct types of freezing have been recognized.

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I. INTRODUCTION

A study of the supercooling and freezing of water has been under way at the National Bureau of Standards for about a year. It was undertaken for the purpose of getting first-hand information as to the way water behaves when supercooled, and as to how one specimen may differ from another, the numerous published reports on the subject being frequently unconvincing and in part conflicting.

As it has become necessary to lay this work aside for a time, it seems well, although the study is still in the exploratory stage, to publish now a brief statement of some of the observations that have

been made and of the inferences drawn therefrom, especially as they are in part contrary to widely held beliefs. Detailed publication must await the completion of the work.

II. THEORIES AND BELIEFS

The theories of crystallization that have found favor and are being upheld are of two types.

According to one type of theory, freezing is initiated by certain molecular aggregates of H_2O, often called ice molecules, which are supposed to exist in water even at scores of degrees above the normal melting point of ice. The number of such ice molecules, relative to the other molecules, is small at the higher temperatures and increases as the temperature is lowered; at each temperature it has a fixed value when equilibrium exists. But opinions differ regarding the time that is required for reestablishing equilibrium after an abrupt change in temperature. Some think that adjustment occurs with great rapidity, practically instantaneously; others have claimed that it requires hours, or perhaps days. These ice molecules tend to cohere, forming aggregates that grow with a finite velocity which increases with the temperature, until a certain size, determined by the temperature, is reached, or until the size becomes such that the aggregate can appropriate to itself the adjacent liquid molecules, converting them into ice molecules in the process. Then freezing proceeds apace.

According to the other type of theory, freezing is initiated by foreign solids—by the walls of the vessel or by motes suspended in the water. The initiation is a boundary phenomenon. The motes or isolated spots on the walls serve as nuclei about which ice is built up until presently a stage is reached at which ordinary rapid freezing begins. The details differ from those of the other type of theory mainly in that in this the initial nuclei are solids foreign to the water, whereas in that they are ice molecules formed from the water itself.

Many observations, mainly on organic compounds, have been cited in confirmation of each type of theory, and it seems not impossible that the two theories may correspond to the opposite sides of a single shield, each being satisfactory under certain conditions. Unfortunately, advocates of the ice-molecule type of theory, at least as applied to water, have seldom, if ever, given sufficient consideration to the possible effect of motes.

Each of these types of theory suggests that the duration of cooling plays an important part in determining the temperature at which spontaneous freezing occurs, and that the same may be true of the immediately preceding thermal history of the water. Observations, not entirely convincing, have been advanced in support of each of these conclusions; and each is widely believed. It is also commonly believed that it is difficult to supercool water by more than a few degrees, and that if any considerable supercooling is to be obtained it is necessary to work with very small volumes (not over a few cubic millimeters) and to protect the water from all kinds of mechanical disturbances. Not a few also believe that the effect of motes is largely a specific one, determined by some chemical or crystallic relation between the mote and ice.

Under the conditions of the present work, none of these widely held beliefs is true, unless it be the last, which has been considered only incidentally. But the results obtained indicate that specificity need not be the determining factor.

III. METHOD AND RESULTS

1. METHOD

The present work was done in this manner: Each specimen of water to be studied was contained in a cylindrical glass bulb with hemispherical ends, from one of which extended axially a 7-mm tube through which the water was introduced. This tube was then sealed by fusion at a point a centimeter or two above the bulb. The bulb proper was 2 cm in diameter by 4 cm long, and was about half filled by the specimen. Total volume of a bulb is 16 to 17 $cm.^3$ The bulbs were carefully cleaned before the water was placed in them. The sealed bulb was placed in a harness of light copper wire, and was suspended in alcohol which was cooled as desired. The temperature of the alcohol was determined by a mercury thermometer (1° C corresponding to 1.7 mm), and was varied not faster than a few tenths of a degree per minute during the several minutes immediately preceding the freezing of the water. It is assumed that under such conditions the significant temperature of the water at the initiation of freezing may be taken as that of the alcohol.

2. GLASS

Both soft glass and Pyrex have been used for the bulbs. There was no indication that the nature of the glass affected the phenomenon.

3. SPONTANEOUS-FREEZING-POINTS

As the temperature of the water is gradually lowered, a point is reached at which a new phase (ice) suddenly appears. The presence of this new phase profoundly affects the behavior of the system. It causes freezing to proceed at all temperatures below 0° C, even though they are higher than that at which the new phase first appeared; but at these higher temperatures the freezing occurs solely at the interface between the ice and the liquid, the ice grows into the liquid. At the lower temperature the liquid specimen freezes spontaneously; at the higher one it is frozen by the ice. The distinction between the active and the passive attitudes of the liquid specimen seems to be worth maintaining. In view of the great latent heat of fusion of ice, it is obvious that the amount of ice initially formed—more exactly, that present a fraction of a second after the specimen has spontaneously frozen—represents only a fraction of the specimen, a fraction depending upon the extent of the supercooling.

In this work our prime concern is with the behavior of the system up to and including the initial appearance of ice.

It has been found that each definite specimen has in general a characteristic temperature, below 0° C, at which it freezes spontaneously. That characteristic temperature will be called the spontaneous-freezing-point of the specimen. It is quite reproducible, and within a fraction of a degree is the same whether: (1) The bulb at room temperature is cooled slowly to 0° C, held at that temperature for 2 or 3 hours, and then cooled to its spontaneous-freezing-point at such a rate as to insure that the temperature of the water never differs materially from that of the bath, or (2) the bulb with frozen water is removed from the bath, the ice melted by suspending the bulb in a bath at +3° C, and the bulb at once returned to the cold bath, now a little

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above the spontaneous-freezing-point of the specimen, and cooled to freezing, or (3) the bulb at room temperature is plunged at once into a bath that is only slightly above the spontaneous-freezing-point of the specimen, and then cooled to freezing. The spontaneous-freezing-point of the specimen remains the same not only for successive freezings on the same day, but for day after day, for weeks or even months, except that there may be a slow progressive change, usually downwards, extending over long periods. See table 1. Such results have been obtained for specimens of water from many sources, both natural and artificial, freezing at various temperatures throughout the range −3 to −15° C, and may be regarded as representing the normal behavior of water under the conditions realized in this work. Some of the specimens were air-free; most of them were saturated with air at atmospheric-pressure. The difference is not of present significance.

TABLE 1.—*Illustrating the regularity of the spontaneous-freezing-point*

[Temperature of spontaneous freezing is t° C]

Bulb CIII				Bulb C23			
Date	t	Date	t	Date	t	Date	t
Jan. 5	−14.9	Mar. 10	−15.4	Feb. 17	−5.8	Mar. 9	−5.9
Do	−15.0	Do	−15.9	Do	−5.9	Do	−5.9
Jan. 29	−15.5	May 14	−16.9	Do	−6.0	Mar. 22	−6.0
Do	−15.3	Do	−16.8	Do	−6.0	Do	−5.9
Feb. 25	−15.7	Do	−16.8	Feb. 24	−6.1	Apr. 22	−5.8
Do	−15.7			Do	−6.1	Do	−5.9
Do	−15.5			Mar. 9	−6.0		

Furthermore, such bulbs of water have been kept continuously below 0° C for 30 days without freezing, the temperature varying between −3 and −12° C, and averaging about −6° C.

Whence, it is evident that neither the length of time that a specimen is held at a low temperature nor the recently past thermal history of the water within the range from room temperature to the specimen's spontaneous-freezing-point is of any prime importance in the freezing of these specimens. Also, in an attempt to supercool water it is unnecessary either to limit one's self to excessively small volumes of water or to protect the water carefully from mechanical disturbances, for without such protection and with volumes as large as 8 cm³ supercooling to −21° C has been observed in this study.

Although the spontaneous freezing of a specimen normally occurs at a definite, fixed, characteristic temperature, departures from that rule are not infrequent. They are of the following four main types, which may be superposed: (1) The first few freezings after the sealing of the bulb may be discordant with later freezings; the specimen may not at once settle down to its normal condition. (2) When studied over a period of weeks, it may be found that the spontaneous-freezing-point of a specimen slowly drifts, usually downwards. In some cases the direction of drift reverses after a time, and later on it may reverse again. (3) A specimen may exhibit an abrupt and permanent change in its spontaneous-freezing-point. In observations extending over weeks, several such abrupt changes, each lasting for several days, may be observed; they may, or may not, be cumulative. (4) The

spontaneous-freezing-point of a specimen may be essentially erratic over a long period, and such a period of irregularity may be, but is not necessarily, adjacent to a period during which the spontaneous-freezing-point remains constant. Erratic behavior seems to be peculiar to those specimens that at some stage of their history have been capable of being supercooled to a low temperature, such as −16° C or lower.

4. MOTES ARE EFFECTIVE

The existence of such abnormalities indicates that the behavior with which we are dealing depends greatly upon something other than the water itself, upon what we may call motes, contained in the water. And the fact that the spontaneous-freezing-point of a given specimen may change abruptly as well as drift, shows that the spontaneous-freezing-point is affected by something other than the mere chemical composition and the gross mass of all the mote material contained in the specimen. But without other evidence one can draw no valid conclusion as to whether the spontaneous-freezing-point is also affected by the chemical or the crystallic state of the motes.

TABLE 2.—*Spontaneous-freezing-points of various waters*

With three exceptions, which are noted, each entry refers to a different specimen of water. The water spontaneously freezes at t° C.

Source or kind of water	t	Source or kind of water	t
Pool, alga-covered, bottom layer	−3.3	Aquarium, midlayers, away from walls and weeds	[b]−11.5
Pool, alga-covered, midlayer	−3.4	Distilled water, ordinary	−11.8
Brook, swift and clear	−3.9	Do	−12.0
Pool, stagnant	−4.1	Residue from glass boiler (No. 1)	−12.2
Spring, small, not recently cleaned	−4.3	Conductivity water	−13.1
Snow-water of winter of 1935-36	−4.6	Residue from glass boiler (No. 2)	−13.9
River, clear	−4.8	Vacuum distilled, no ebullition	−14.3
Spring, large, strong flow, fairly clean	−5.1	Hot-water supply, country, heated by water-back stove	−14.4
Snow-water, Feb. 1937, many surface motes	−5.9	Distilled water, ordinary, heated to 97° C for 36 hr	−15.0
Washington City water, cold-water faucet	−6.0	Conductivity water, heated to 97° C for 36 hr	−15.4
Pool, alga-covered, surface layer	−6.0	Vacuum distilled, no ebullition	−15.6
Washington City water, hot-water faucet [a]	−6.2	Distilled water, ordinary, old stock	−15.8
Do [a]	−6.5	Conductivity water	−16.0
Ice-water, melted commercial ice	−7.0	Vacuum distilled from chromic solution, no ebullition	−18.0
Aquarium, from surface of wall and of weeds	−7.4	Vacuum distilled, no ebullition	[c]−18.5
Water tank, country, cold	−7.5	Do	[c]−20.2
Distilled water, ordinary, new stock	−7.6	Vacuum distilled from chromic solution (same as −18.0°)	−21.1
Snow-water, Feb. 1937, few surface motes	−7.7		
Well, deep, iron pump	−7.9		
Aquarium, midlayers, away from walls and weeds	[b]−10.6		
Conductivity water	−10.7		
Distilled water, ordinary, old stock	−10.8		
Snow-water, Feb. 1937, midlayers	−10.9		

[a] The water from this faucet is never really hot.
[b] One freezing of this specimen gave −10.6° C, a following one gave −11.5° C; each is entered in the table.
[c] These two entries refer to the same specimen.

Some light, however, is thrown upon this question by the observations assembled in a study of 37 specimens of water obtained from various sources, and freezing at temperatures ranging from −3.3 to −21.1° C. These specimens arranged in the order of their spontaneous-freezing-points, each on the day of the last observation preceding the tabulation, are briefly described in table 2. For three of the specimens the observations on that day were widely spread; for them each of the individual determinations is tabulated. If the action of a mote were a specific one—depending upon its relation,

chemical or crystallic, to ice—then one might expect to find that the spontaneous-freezing-points of the several specimens form a discontinuous series, being grouped about a few widely separated temperatures. In table 2 there is no clear evidence of any such grouping. This does not justify one in concluding that no specific effect is involved, but it does indicate that if it is involved, then in this work it is quite completely overshadowed by one or more other effects, probably those responsible for the abnormal behaviors already mentioned.

5. HEATING

It has long been known that the extent to which a substance can be supercooled may in certain cases be increased by a preliminary heating of the melt to a temperature well above the melting point; and that the increased supercooling so obtained increases, within limits, with the maximum temperature to which the melt is heated, and survives several successive freezings and meltings. There seems to be no generally accepted explanation of this effect, and although I have not looked into the subject as carefully as I desire, I am of the impression that it is commonly believed that this effect of heating is temporary, that it will ultimately vanish if the substance is held at a temperature somewhat above its melting point. Such a belief is entirely rational if the effect be due (1) to a destruction of preexisting ice molecules, or (2) to a change in the adsorption, either of the motes on the walls or of the water on the motes or on the walls, or (3) to a complete melting or solution of some of the motes of certain crystal forms.

In each of those three cases, it is entirely thinkable that the time required for ice to begin to form after the specimen has been cooled to its spontaneous-freezing-point, assumed to be a definite temperature, may be increased by the partial destruction, by heating, of the corresponding condition, and may increase progressively with that destruction. But it is not clear how that temperature can depend upon the mere extent of any one of those conditions. It seems more reasonable to expect that the spontaneous-freezing-point would remain unchanged until the pertinent condition shall have completely vanished, and that it then would jump abruptly to its new value.

TABLE 3.—*Effect of heating on the spontaneous-freezing-point*

Each heating is indicated in its proper chronological position, and by the maximum temperature and the length of time that that temperature was maintained. Except while being heated or frozen, the bulb (C35) was at room temperature; the water froze spontaneously at t° C.

Date	t	Date	t	Date	t	Date	t
Mar. 4	−6.2	Mar. 27	−6.9	97° C, 2 hr		June 29	−14.0
Mar. 8	−6.1	Do	−7.2	Apr. 3	−13.8	Nov. 16	−14.1
Do	−6.0	Mar. 29	−6.8	Apr. 7	−13.7	Do	−13.7
Mar. 22	−6.2	97° C, 2 hr		97° C, 5.5 hr		Dec. 11	−13.4
Do	−6.2	Mar. 30	−13.0	Apr. 10	−13.8	Do	−13.4
54° C, 8 hr		Do	−12.9	Do	−14.0		

But observations, both old and new, indicate that the spontaneous-freezing-point changes progressively with the heating—within limits, heating to a lower temperature produces less effect than does heating to a higher one, and heating for a shorter time produces less effect than does heating for a longer one. This is illustrated by the data contained in table 3, which also show that the effect of heating is

largely a permanent one, and that after the specimen has been heated to a certain temperature for some time, additional heating to that same temperature may produce no additional effect, a steady state having been reached. Such a progressive change is difficult to explain if it arises from any of the three effects of heat already mentioned, and the same is true of the permanency of the change.

6. EFFECT OF SIZE OF MOTES

But there is a fourth possible effect. Heating the melt may cause the motes to dissolve in it. That will reduce their number and their size. As before, it is hard to see how a change in the mere number of motes per unit of volume can affect the spontaneous-freezing-point. And that it actually does not, seems to be indicated by the fact that the observed spontaneous-freezing-point of a mixture is the same as that of the higher-freezing constituent; e. g., one containing 10 percent of water freezing at −7° C, and 90 percent of water freezing at −15° C froze at −7° C.

But a change in the size of the motes may cause a change in the spontaneous-freezing-point; and the size will vary progressively, and so does the spontaneous-freezing-point. The idea that the spontaneous-freezing-point may be closely associated with the size of the motes and, within limits, may vary progressively with it, is consistent not only with the observed effect of preheating the melt, but also with the observed tendency of the spontaneous-freezing-point of a specimen to drift slowly to lower temperatures, the motes presumably dissolving slowly while the bulb is kept at room temperatures. The same idea offers an explanation of the erratic behavior of certain of the specimens, as the size of the motes may increase by coalescence, and decrease by dispersion, and be varied by solution and precipitation. It also offers a ready explanation of the almost continuous distribution of the spontaneous-freezing-points listed in table 2. The idea that the size of the motes may be the significant variable in this work is very alluring and deserves careful consideration.

7. SEDIMENTATION

If the size of the motes is the significant variable, then the spontaneous-freezing-point of a given lot of water should be subject to change by sedimentation. Indeed, in table 2 it may be seen that a new stock of distilled water, well stirred by drawing it from the still into the stock bottle, had a spontaneous-freezing-point of −7.6° C, whereas old stocks that had been undisturbed for some days or perhaps weeks froze at −10.8° C in one case, and at −15.8° C in another. Although very suggestive this is not conclusive, as there is no evidence that the old stocks would have frozen at a higher temperature before they had settled; the observations having been made for another purpose, the records are not sufficient for our present one. But other experiments were made. Sedimentation tubes from which water could be drawn from various levels without stirring the remainder of the water were set up. The spontaneous-freezing-point of the stirred distilled water placed in them was determined, and after the tubes had remained undisturbed at room temperatures for 2 or 3 weeks, samples were drawn and frozen. Bulbs of the same kind as those already described were used, but the necks were closed by ground-on caps, not by fusion. Several experiments were made, and in some cases no evidence of any

change due to sedimentation was found. But in view of the very significant observations recorded in table 4, it is believed that faulty technique is responsible for the negative results. That will be investigated when the work is renewed.

TABLE 4.—*Effect of sedimentation*

In the first section of the table are given the observed values of the spontaneous-freezing-point of the water that was placed in the sedimentation tube. Two weeks later a sample was drawn from the topmost layers and another from the very bottom of the tube, and their spontaneous-freezing-points (t° C) were determined. These are given in the other two sections of the table.

Initial		Top		Bottom	
Time	t	Time	t	Time	t
May 21, 2:19 p. m.	−12.0	June 3, 3:34 p. m.	−12.7	June 4, 3:17 p. m.	−7.8
2:37 p. m.	−12.7	3:49 p. m.	−12.6	3:24 p. m.	−7.3
2:50 p. m.	−12.0	June 4, 9:56 a. m.	−13.0	4:21 p. m.	−9.1
May 22, 11:34 a. m.	−12.2	10:05 a. m.	−12.7	4:35 p. m.	−10.5
11:46 a. m.	−12.2			4:44 p. m.	−10.8
		Mean	−12.8	June 8, 1:26 p. m.	−11.7
Mean	−12.2			1:36 p. m.	−12.0
				1:47 p. m.	−12.1

From table 4 it may be seen that after settling for 2 weeks the spontaneous-freezing-point of the topmost layers is only slightly lower than that of the initial water. Considered alone, this might be taken as an indication that no settling has occurred. But such a conclusion is inconsistent with the values obtained for the bottom layers. For them the spontaneous-freezing-point is at first nearly 5° C higher than that of the initial water, and the difference between the two decreases with successive freezings until it finally becomes zero. This entirely unexpected behavior is in complete accord with the idea that the spontaneous-freezing-point is determined by the size of the motes. As the motes settle on the bottom of the tube, they cohere, forming larger aggregates. The size of these aggregates in the sample drawn from the bottom was at first almost that which corresponds to a spontaneous-freezing-point of −7.5° C. With successive freezings, these loosely bound aggregates were gradually broken up, and the spontaneous-freezing-point fell, continuously approaching the value characteristic of the original water. The close accord between the spontaneous-freezing-points of the topmost layers and of the initial water does not indicate that there has been no sedimentation, but merely that sedimentation had not progressed so far as to have removed from those layers all motes of such a size as to cause spontaneous freezing at −12.8° C.

Much of the preceding has been written as though the motes in a given specimen of water are all of the same size. Obviously, such will not in general be the case; they will differ greatly in size. But according to the idea being developed, the spontaneous-freezing-point will be determined, insofar as the size of the motes is the significant quantity, by the size of the largest mote present, provided that that size does not exceed a value still to be determined. The actual number of such motes that is present in a unit volume of the water is of little or no importance, as has already been shown.

8. AGITATION

That it has been found unnecessary to take any special precaution to protect these bulbs from mechanical disturbances while in the supercooled condition, has been mentioned. But one can go much further. For example, if a bulb containing water that freezes at $-15°$ C be cooled to $-14°$ C, it can at that temperature be tipped about with impunity, pouring the cold water over all its interior surface, without causing the water to freeze. But the water will freeze instantly if the bulb be treated thus: Holding the top of the neck of the bulb between the thumb and index finger of the right hand, the bulb being vertical and neck up, strike the right hand sharply downward against the left.

Even sharp strokes of a cold metal rod against the outside of a stationary supercooled bulb have failed to cause the water to freeze. On the other hand, an exceedingly gentle wiping of the glass-water interface, well below the free surface of the water, may sweep off tiny flakes of ice—that is, may initiate freezing—when the temperature is only a few degrees below 0° C and well above the spontaneous-freezing-point of the water, which in these tests was contained in an open test tube. In neither case are my experiments extensive enough to justify a more definite statement.

9. TYPES OF FREEZING

If a bulb of water at room temperature be plunged into a bath cooled well below the spontaneous-freezing-point of the water, then freezing will begin at the walls before the entire volume of water shall have been reduced to its spontaneous-freezing-point, and will proceed gradually from the walls inward. The resulting ice may be quite clear.

If the bulb be placed in a bath at a temperature above the spontaneous-freezing-point of the water, and if the temperature be progressively lowered in such a manner that when the spontaneous-freezing-point shall have been reached the temperature of the water will be essentially the same throughout, then the water will freeze throughout in the twinkling of an eye, forming a solid translucent mass. Although only a small fraction of the water is actually ice at the instant after freezing sets in, the ice crystals are so numerous and intermingled and are distributed so uniformly throughout the volume that the whole is locked together into a single solid mass. Such is the behavior of the bulbs so far studied. The freezing might proceed more slowly and the ice might be clearer if the number of the motes responsible for the freezing at that temperature were small, say if only one were present.

An approximation to the case of a single mote may be obtained by placing into the water a well washed bit of a suitable solid. For example, such a bit of solid was placed in water that froze at $-13.6°$ C; freezing then began at the solid at $-6.7°$ C, and visibly progressed from the solid outward into the water.

IV. SUMMARY

For specimens of water sealed in glass bulbs the following facts have been established:

1. The liquid specimen normally freezes spontaneously at a definite temperature, here called the spontaneous-freezing-point, characteristic of the specimen.

2. For no specimen yet examined has the spontaneous-freezing-point been so high as 0° C.

3. Abnormal behavior, in which the spontaneous-freezing-point is not constant and may even be erratic, is not uncommon.

4. The lowering of the spontaneous-freezing-point by preheating the liquid is a lasting effect, persisting for months.

5. Sedimentation may change the spontaneous-freezing-point.

6. All of these effects are consistent with the idea that the spontaneous-freezing-point is determined by motes suspended in the water, and in particular by the size of the largest mote present, provided that that size does not exceed a value yet to be determined.

7. Extreme supercooling is not dependent upon the use of a diminutive volume of water.

8. Extreme quiescence is not at all essential to supercooling. Indeed, supercooled water may sustain a considerable mechanical disturbance without freezing.

9. A very gentle wiping of a glass-water interface may initiate freezing when the temperature is only slightly below 0° C, although the spontaneous-freezing-point of that specimen of water is much lower.

10. A volume of water as great as 8 cm^3 has been repeatedly cooled, without precautions to avoid mechanical disturbances, to −21° C. without its freezing.

11. Three types of freezing have been distinguished.

Of these items, 1, 4, 5, 7, and 8 are contrary to widely held opinions, although 8 accords with certain Swiss observations recorded nearly 80 years ago.

The work is still in its preliminary stages. Much remains to be done, some of it extremely obvious. We hope that it will be possible to resume the work at no very distant date.

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THERMAL EXPANSION AND EFFECTS OF HEAT TREATMENTS ON THE GROWTH, DENSITY, AND STRUCTURE OF SOME HEAT-RESISTING ALLOYS

By Peter Hidnert

ABSTRACT

Coefficients of linear expansion for various temperature ranges between 20 and 1,000° C were obtained on some new heat-resisting alloys: An iron-chromium-aluminum alloy and three iron-chromium-aluminum-cobalt alloys. No polymorphic transition was observed in these alloys between 20 and 1,000° C. The alloys exhibited growth (0.82 to 2.81 percent) after various heat treatments at temperatures up to 1,400° C. Additional heat treatments would probably cause additional growth. The densities of the mechanically worked iron-chromium-aluminum alloy and iron-chromium-aluminum-cobalt alloys increased 1.12 to 2.50 percent as a result of various heat treatments to 1,400° C. Tremendous grain growth occurred in the heat-resisting alloys as a result of various heat treatments at elevated temperatures.

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I. INTRODUCTION

The commercial alloys used for electric heating are primarily nickel-chromium and nickel-chromium-iron alloys. Recently, however, a new series of heat-resisting alloys composed primarily of iron and chromium with smaller additions of aluminum or aluminum and cobalt, has been developed. These alloys can be heated to higher temperatures than the nickel-chromium and iron-nickel-chromium alloys, but they have disadvantages which will be indicated later.

In 1931, data [1] [1] on the linear thermal expansion of nickel-chromium, iron-chromium, and nickel-chromium-iron alloys were published. The present paper gives the results obtained in an investigation on the thermal expansion of the new heat-resisting alloys: Iron-chromium-aluminum alloy and iron-chromium-aluminum-cobalt alloys. Samples

[1] The numbers in brackets here and elsewhere in the text refer to the references at the end of this paper.

of these alloys were secured through the cooperation of two companies.[1]

Measurements were made of the linear thermal expansion of the alloys at various temperatures between 20 and 1,000° C. The effects of various heat treatments between 1,000 and 1,400° C on the growth, density, and structure of these alloys, were also investigated. It is expected that these data will be useful to engineers, metallurgists, physicists, and others in the applications of these alloys; for example, in the design of equipment for high-temperature processes.

II. MATERIALS INVESTIGATED

Four samples of heat-resisting alloys (iron-chromium-aluminum and iron-chromium-aluminum-cobalt) were investigated. Table 1 gives the trade names, chemical compositions, heat treatments, etc.

[1] The author expresses his appreciation for the cooperation by C. O. Jelliff Mfg. Corporation, Southport, Conn., and Hoskins Mfg. Co., Detroit, Mich. These companies furnished the samples of heat-resisting alloys and information about their preparation.

TABLE 1.—*Chemical composition and heat treatment of heat-resisting alloys*

TABLE 1.—*Chemical composition and heat treatment of heat-resisting alloys*

Sample	Trade name	Chemical composition [a]							Heat treatment	Cross-section of sample	Manufacturer	Remarks by manufacturer
		Cr	Al	Co	Fe [b]	Mn	Si	C				
		(a) IRON-CHROMIUM-ALUMINUM ALLOYS										
		Per-cent	*Per-cent*	*Per-cent*	*Per-cent*	*Per-cent*	*Per-cent*	*Per-cent*				
1586	Hoskins' Alloy No. 10.[c]	38.6	7.9	------	53.1	0.17	0.19	0.05	Hot-rolled	¼-in. diam.	Hoskins Mfg. Co.	Hoyt and Archer [2] stated that an object of their invention was to provide an alloy of such properties as to be suitable for the fabrication of cast or wrought articles which are exposed to oxidizing conditions at elevated temperatures, such as annealing or carburizing boxes, or parts entering into the construction of conveyors, heat exchangers, recuperators, or other mechanism exposed to the action of oxidizing atmospheres at elevated temperatures. Another object was to provide an alloy suitable for the construction of electrical resistance elements capable of operating at high temperature with a long life.
		(b) IRON-CHROMIUM-ALUMINUM-COBALT ALLOYS [d]										
1579	Kanthal A	23.4	6.2	1.9	68.5	------	------	0.06	Hot-rolled	0.324 in. diam.	C. O. Jelliff Mfg. Corp.	Suitable for temperatures up to 1,300° C (2,370° F). Principal uses are: Industrial furnaces, electric-range units, other domestic appliances requiring high temperatures, high-grade spark plugs, Diesel-engine glow plugs and oil-burner ignition points.
1580 [e]	Kanthal A1	23.4	5.7	1.9	69.0	------	------	.06	Cold-rolled	¾ by 0.104 in.	------do------	Used mainly for industrial furnaces operating at high temperatures up to 1,350° C (2,460° F).
1581	Kanthal D	22.6	4.5	2.0	70.9	------	------	.09	Hot-rolled	$2\frac{1}{64}$-in. diam.	------do------	Suitable for temperatures up to 1,150° C (2,100° F) and has the same range of operation as nickel-chromium alloys.

[a] Chemical analyses were made on pieces cut from both ends of each sample after the thermal-expansion determinations had been completed.
[b] Percentage of iron determined by difference.
[c] Same as Smith Alloy No. 10 (see Hoyt and Scheil [5]).
[d] Kantzow [3], the inventor of Kanthal alloys, stated that "his invention makes it possible to obtain alloys having, in most cases, better properties than those of the Nichrome, at a considerably lower price than that of the latter."
[e] Received in bent condition; straightened in vise before thermal-expansion determinations.

III. THERMAL-EXPANSION APPARATUS

The samples of heat-resisting alloys were investigated with the precision comparator type of thermal-expansion apparatus described by Souder and Hidnert [4]. The white furnace shown at the left of figure 1 of their publication was used for temperature ranges between 20 and 1,000° C. Figure 4 of the same publication shows the details of mounting the samples in the furnace.

Platinum-osmium observation wires (6½ percent of osmium) were used in all tests of the samples except sample 1579. For this sample, platinum-iridium observation wires (20 percent of iridium) were used. The diameter of each observation wire was 0.050 mm. A vane weighing 18 g was attached at the bottom of each observation wire which was in contact with samples 1579 and 1581. In order to reduce the possibility of breakage of the observation wires at elevated temperatures, lighter vanes (each weighing 9 g) were used with the other samples.

IV. THERMAL EXPANSION OF HEAT-RESISTING ALLOYS

The samples of heat-resisting alloys were arranged in two groups, as indicated in section II. The samples used for thermal-expansion determinations were 300 mm in length. Each expansion curve was plotted from a different origin in order to display the individual characteristics of each curve. Results obtained in a second test represent data on material after the heat treatment incident to the first test.

1. IRON-CHROMIUM-ALUMINUM ALLOY

Two expansion tests were made on a hot-rolled iron-chromium-aluminum alloy (sample 1586). The observations obtained on heating and cooling the sample at various temperatures between 20 and 1,000° C. are shown in figure 1. The observations on cooling in the first test lie appreciably below the expansion curve. In the second test, the observations on cooling are very close to the expansion curve.

Table 2 gives coefficients of expansion which were derived from the curves in figure 1. This table also shows the difference in length before and after each expansion test.

The average coefficients of expansion of the iron-chromium-aluminum alloy, after heat treatment incident to the first test, are slightly greater than the coefficients of the hot-rolled alloy.

TABLE 2.—*Average coefficients of linear expansion of hot-rolled iron-chromium-aluminum alloy*

[Fe 53.1, Cr 38.6, Al 7.9, percent]

Test [a]	Average coefficients of expansion per degree centigrade											Change in length after heating and cooling [b]
	20 to 60° C	20 to 100° C	20 to 200° C	20 to 300° C	20 to 400° C	20 to 500° C	20 to 600° C	20 to 700° C	20 to 800° C	20 to 900° C	20 to 1,000° C	
	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	*Percent*
1H	------	11.4	11.9	12.4	12.7	13.2	14.0	14.6	15.0	15.5	16.0	−0.10
1C	11.9	11.9	12.1	12.4	12.8	13.7	------	------	------	------	17.1	
2H [c]	------	12.0	12.2	12.7	13.1	13.9	14.6	15.4	15.9	16.5	17.1	+.00

[a] H indicates heating and C cooling.

[b] Determined from the expansion curve on heating and the contraction curve (or observation) on cooling. The plus (+) sign indicates an increase in length and the minus (−) sign a decrease in length.

[c] Observations on cooling close to expansion curve on heating.

In 1935, Hoyt and Scheil [5] reported that the coefficient of linear expansion of Smith Alloy No. 10[3] is about 18×10^{-6} per degree C between room temperature and 1,315° C. "This means an expansion of about 0.27 inch per foot, on heating to 2,400 degrees Fahr. (1,315 degrees Cent.). These determinations were made on wire in the life

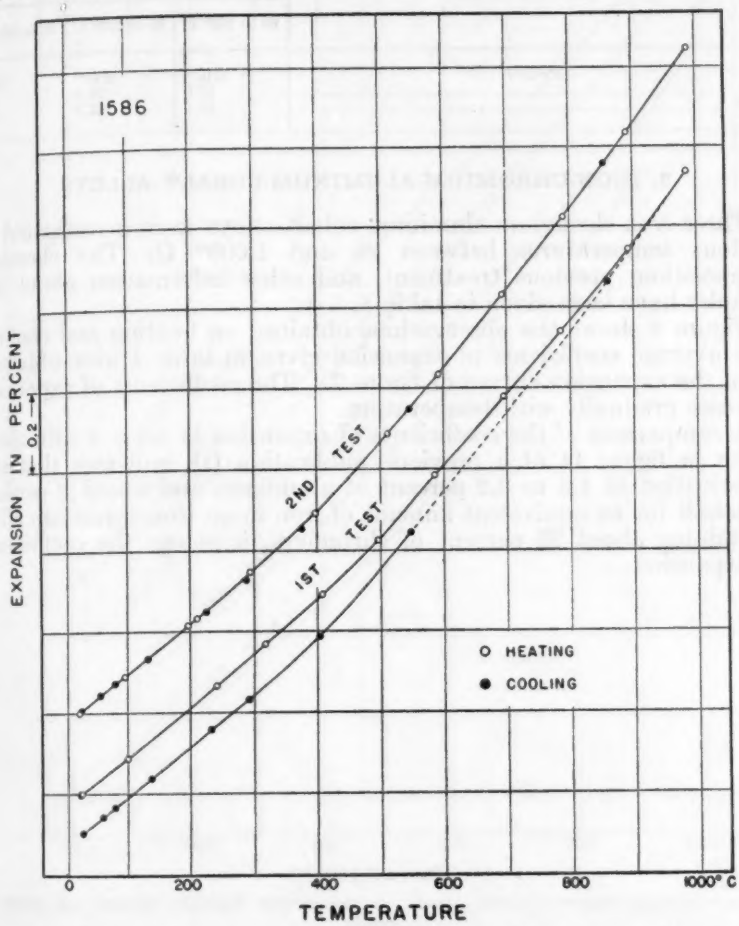

FIGURE 1.—*Linear thermal expansion of hot-rolled iron-chromium-aluminum alloy.*

Fe 53.1, Cr 38.6, Al 7.9, Mn 0.17, Si 0.19, C 0.05 percent.

tester with the Ames dial and are subject to a minor correction when more accurate determinations become available."

Table 3 gives coefficients of expansion of two iron-aluminum alloys investigated by Schulze [6]. From interpolation and comparison of these coefficients of expansion with those given in table 2, it appears that the substitution of approximately 39 percent of chromium for the same amount of iron in an iron-aluminum alloy containing about 8 percent of aluminum, has little effect on the coefficients of expansion for temperature ranges between 20 and 500° C.

[3] Same as Hoskins' Alloy No. 10 (see table 1).

TABLE 3.—*Coefficients of expansion of annealed iron-aluminum alloys*

[Schulze, reference 6]

Aluminum content	Average coefficients of linear expansion per degree centigrade		
	20 to 100° C	20 to 300° C	20 to 500° C
Percent	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$
5.66	12.0	13.0	13.8
10.52	12.2	13.3	14.0

2. IRON-CHROMIUM-ALUMINUM-COBALT ALLOYS

Three iron-chromium-aluminum-cobalt alloys were investigated at various temperatures between 20 and 1,000° C. The chemical composition, previous treatment, and other information about the samples have been given in table 1.

Figure 2 shows the observations obtained on heating and cooling. The average coefficients of expansion given in table 4 were obtained from the expansion curves of figure 2. The coefficients of expansion increase gradually with temperature.

A comparison of the coefficients of expansion in table 4 with those given in figure 11 of a previous publication [1], indicates that the substitution of 4.5 to 6.2 percent of aluminum and about 2 percent of cobalt for an equivalent amount of iron in an iron-chromium alloy containing about 23 percent of chromium, increases the coefficients of expansion.

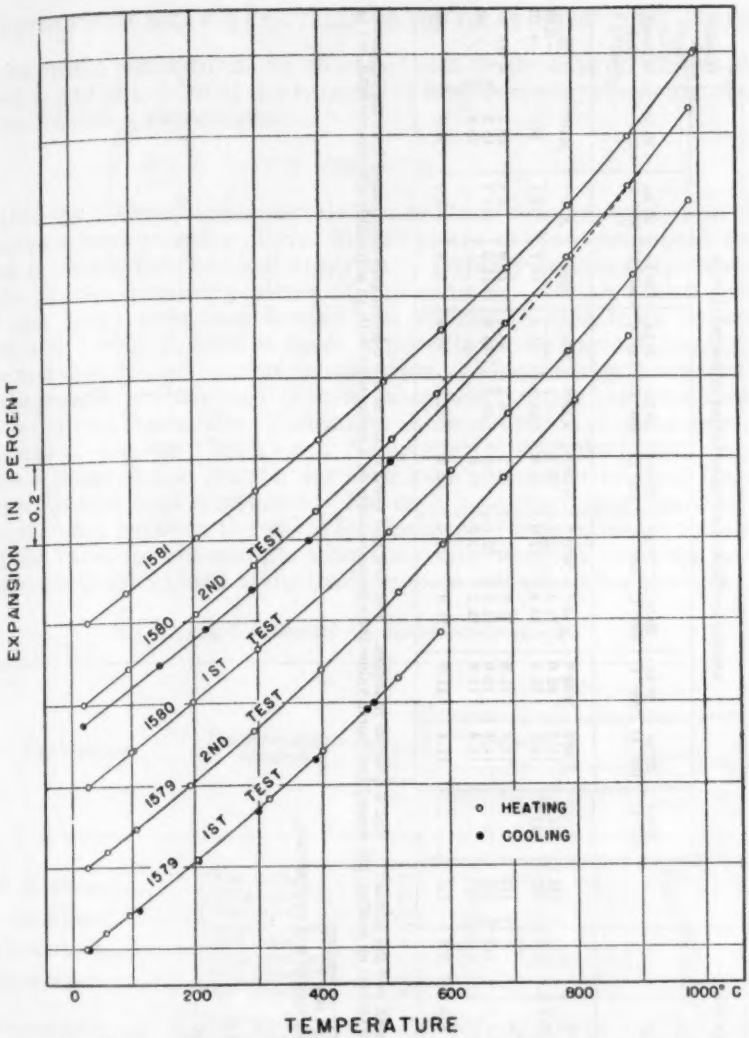

FIGURE 2.—*Linear thermal expansion of three iron-chromium-aluminum-cobalt alloys.*

Sample 1579, Fe 68.5, Cr 23.4, Al 6.2, Co 1.9, C 0.06 percent (hot-rolled).
Sample 1580, Fe 69.0, Cr 23.4, Al 5.7, Co 1.9, C 0.06 percent (cold-rolled).
Sample 1581, Fe 70.9, Cr 22.6, Al 4.5, Co 2.0, C 0.09 percent (hot-rolled).

TABLE 4.—*Average coefficients of linear expansion of iron-chromium-aluminum-cobalt alloys*

Sample	Chemical composition				Test [a]	Average coefficients of expansion per degree centigrade										Change in length after heating and cooling [b]
	Fe	Cr	Al	Co		20 to 60° C	20 to 100° C	20 to 200° C	20 to 300° C	20 to 400° C	20 to 500° C	20 to 600° C	20 to 700° C	20 to 800° C	20 to 900° C	20 to 1,000° C	
	%	%	%	%		×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	%
1579	68.5	23.4	6.2	1.9	1H [c]	11.7	11.5	12.0	12.4	12.7	13.2	13.7	14.4	14.7	15.1	(d)	−0.01
					2H	11.9	11.7	12.0	12.4	12.9	13.4	13.9					+.01
1580	69.0	23.4	5.7	1.9	1H	-------	11.6	11.9	12.2	-------	12.8	13.2	13.6	13.9	14.4	15.1	(e)
					2H	-------	11.5	12.0	12.3	12.6	13.0	13.5	13.8	14.2	14.7	15.3	−.05
					2C	-------	11.4	11.6	12.2	12.5	13.0	-------	-------	-------	-------	15.8	
1581	70.9	22.6	4.5	2.0	1H	-------	11.4	11.6	11.9	12.1	12.4	12.7	13.0	13.4	13.9	14.5	.00

[a] H indicates heating and C cooling.
[b] The plus (+) sign indicates an increase in length and the minus (−) sign a decrease in length. The first and third values in this column were determined from the expansion curve on heating and the contraction curve (or observation) on cooling; the second and fourth values from measurements on a comparator with an adjustable micrometer head, set to an end standard of known length.
[c] Observations on cooling close to expansion curve on heating.
[d] Pt-Ir observation wires broke between 900 and 1,000° C.
[e] Sample warped on cooling. Before second test, sample was straightened.

V. EFFECTS OF HEAT TREATMENTS ON HEAT-RESISTING ALLOYS

The results obtained on the effects of heat treatments on the growth, density, and structure of the samples of heat-resisting alloys are given in the following subsections.

1. GROWTH

After the thermal-expansion determinations were completed on the samples of heat-resisting alloys, 50-mm pieces were cut from both ends of each sample for chemical analyses.[4] Density determinations were made on the remaining pieces of the samples. These pieces (each 200 mm long) were then heated [5] to various temperatures between 1,100 and 1,400° C, held at these temperatures for various lengths of time and then cooled to room temperature. Measurements were made on the growth (or shrinkage) of these samples after each heat treatment. Table 5 shows the results obtained on these samples and on samples of Chromel A (sample 1292A) and Nichrome IV (sample 1293). Each value represents the growth (or shrinkage) from the original length before the first heat treatment. For each heat treatment, one-half of the difference between the value for the sample with oxide on the ends and the value for the sample with the oxide removed from the ends, represents the thickness of the oxide or scale on each end of the sample.

TABLE 5.—*Growth of heat-resisting alloys*

Heat treatment	Condition of ends of sample	Growth [a]					
		Fe-Cr-Al; sample 1586	Fe-Cr-Al-Co			Chromel A; sample 1292A	Nichrome IV; sample 1293
			Sample 1579	Sample 1580	Sample 1581		
		Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
1,100° C for 24 hours	With oxide	−0.01	−0.02	+0.00	−0.00	+0.00	+0.01
	Oxide removed	−.01	−.02	+.00	−.00	−.01	−.00
1,150° C for 24 hours	With oxide	−.00	−.02	+.02	+.03	−.01	+.02
	Oxide removed	−.00	−.02	+.01	+.02	−.03	−.01
1,200° C for 24 hours	With oxide	+.02	+.00	+.08	+.08	−.03	+.04
	Oxide removed	+.01	−.01	+.08	+.07	−.05	+.00
1,250° C for 24 hours	With oxide	+.05	+.03	+.14	+.19	−.06	+.04
	Oxide removed	+.03	+.01	+.11	+.18	−.08	+.02
1,300° C for 24 hours	With oxide	+.10	+.12	+.18	+.35	−.04	+.11
	Oxide removed	+.09	+.10	+.17	+.33	−.15	+.03
1,350° C for 24 hours	With oxide	+.18	+.24	+.41	+.61	+.07	+.25
	Oxide removed	+.17	+.23	+.38	+.57	−.12	−.04
1,350° C for 4 additional days	With oxide	+.38	+.51	+.90	+.95	----------	----------
	Oxide removed	+.35	+.49	+.87	+.91	----------	----------
1,350° C for 3 additional days	With oxide	+.56	+.79	+1.58	+1.80	----------	----------
	Oxide removed	+.54	+.77	+1.55	+1.73	----------	----------
1,400° C for 5 hours	With oxide	+.69	+.91	+1.97	+2.09	----------	----------
	Oxide removed	+.69	+.90	+1.96	+2.08	----------	----------
1,400° C for 5 hours (2d time)	With oxide	[b] +.82	+1.09	+2.41	+2.50	----------	----------
	Oxide removed	[c]	[c]	[c]	[c]	----------	----------
1,400° C for 5 hours (3d time)	With oxide	----------	+1.21	+2.75	+2.81	----------	----------
	Oxide removed	----------	[c]	[c]	[c]	----------	----------

[a] Each value represents the growth (or shrinkage) from the original length before the first heat treatment.
[b] Sample warped during heat treatment and was broken in attempting to straighten it.
[c] Slight oxide not removed.

[4] Table 1 gives results of chemical analyses.
[5] A platinum-wound tube furnace was used for temperatures between 1,100 and 1,350° C, in which the samples were exposed to air. A gas furnace was used for heating the samples to 1,400° C.

The samples of iron-chromium-aluminum-cobalt alloys indicated the greatest growth. The total growth after the various heat treatments ranged from 1.21 to 2.81 percent. The total growth of the sample of iron-chromium-aluminum alloy was nearly 1 percent. Additional heat treatments would probably cause additional growth of these alloys. A comparison of the growth and the aluminum content of these alloys indicates that the growth decreases with an increase in the aluminum content.

The samples of Chromel A and Nichrome IV scaled at elevated temperatures.

Hoyt and Scheil [5] found that wires of Smith Alloy No. 10 [6] grow when heated to high temperatures. They recommended that an allowance for growth of at least ¼ inch per foot be made, in addition to that for the expansion. This minimum allowance for growth corresponds to 2.1 percent.

2. DENSITY

Density determinations were made on the 300-mm samples of heat-resisting alloys before the thermal-expansion tests were undertaken. After the thermal-expansion tests were completed, 50-mm pieces were cut from both ends of each sample for chemical analyses, and density determinations were made on the remaining pieces of the samples, as stated in the preceding subsection. After various heat treatments on these pieces for determinations of growth, oxide or scale was removed from the entire surface of each sample,[7] and density determinations were made. The densities are given in table 6.

The iron-chromium-aluminum alloy has the lowest density of the heat-resisting alloys investigated. After the heat treatments for the determinations of growth, the samples of heat-resisting alloys indicated appreciable increases in density. These increases in density varied from 1.12 to 2.50 percent.

TABLE 6.—*Density of heat-resisting alloys*

Sample	Chemical composition				Density at 23° C			Change in density [a]
	Chromium	Aluminum	Cobalt	Iron	Before expansion tests	After expansion tests	After heat treatments for determinations of growth	
	Percent	*Percent*	*Percent*	*Percent*	g/cm³	g/cm³	g/cm³	*Percent*
1586 [b]	38.6	7.9	----------	53.1	6.878	6.911	6.955	+1.12
1579	23.4	6.2	1.9	68.5	7.099	7.099	7.200	+1.42
1580	23.4	5.7	1.9	69.0	7.133	7.136	7.311	+2.50
1581	22.6	4.5	2.0	70.9	7.233	7.235	7.334	+1.40

[a] Change from density before expansion tests to density after heat treatments for determinations of growth.
[b] Hoyt and Scheil [5] reported 6.9 g/cm³ for the density of an iron-chromium-aluminum alloy containing about 37.5 percent of chromium and 7.5 percent of aluminum.

As both the densities and the lengths of the samples of heat-resisting alloys increased, the cross-sectional areas of the samples must have decreased as a result of heat treatments to various temperatures up to 1,400° C.

[6] Same as Hoskins' Alloy No. 10 (see table 1).
[7] A small piece was cut from one end of each sample for examination of its structure.

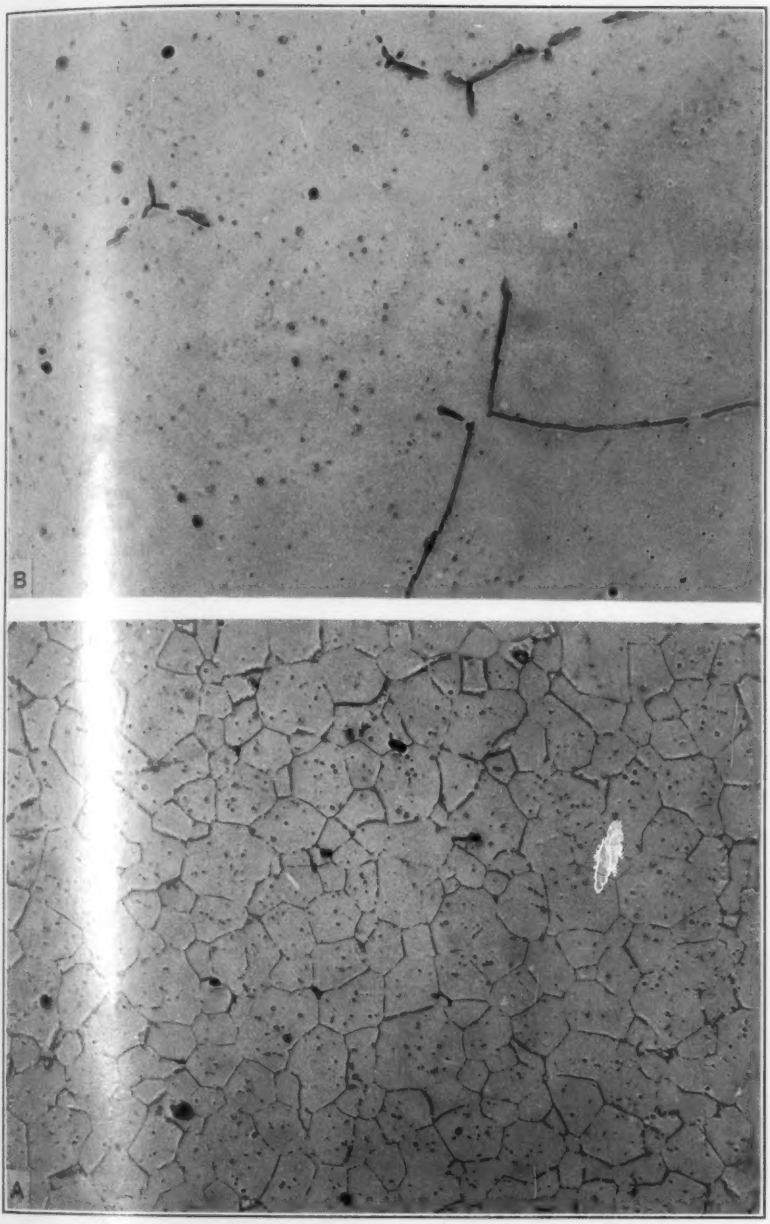

FIGURE 3.—*Microstructure of iron-chromium-aluminum alloy (iron 53.1, chromium 38.6, aluminum 7.9, manganese 0.17, silicon 0.19, carbon 0.05 percent); × 100.*

A. Sample 1586 (hot-rolled), before heat treatments. *B.* Sample 1586, after heat treatments to various temperatures up to 1,400° C.

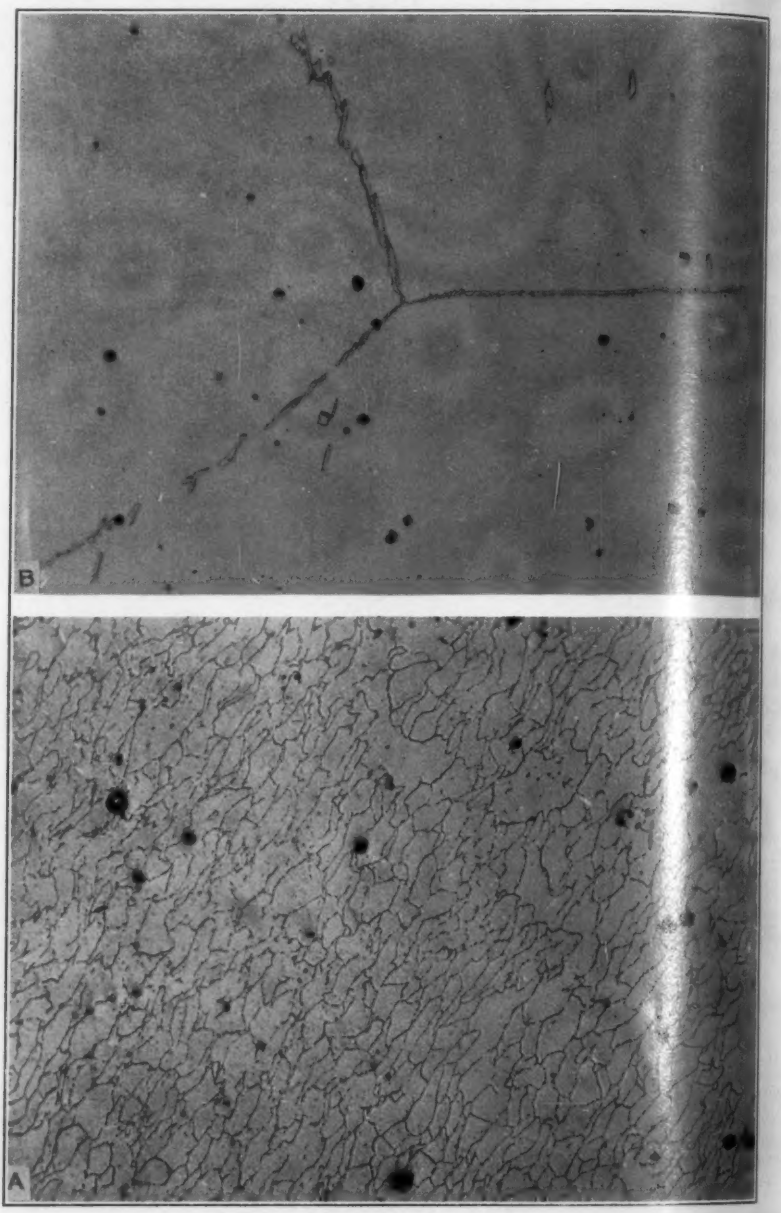

FIGURE 4.—*Microstructure of iron-chromium-aluminum-cobalt alloy (iron 68.5, chromium 23.4, aluminum 6.2, cobalt 1.9, carbon 0.06 percent); × 100.*

A. Sample 1579 (hot-rolled), before heat treatments. *B*. Sample 1579, after heat treatments to various temperatures up to 1,400° C.

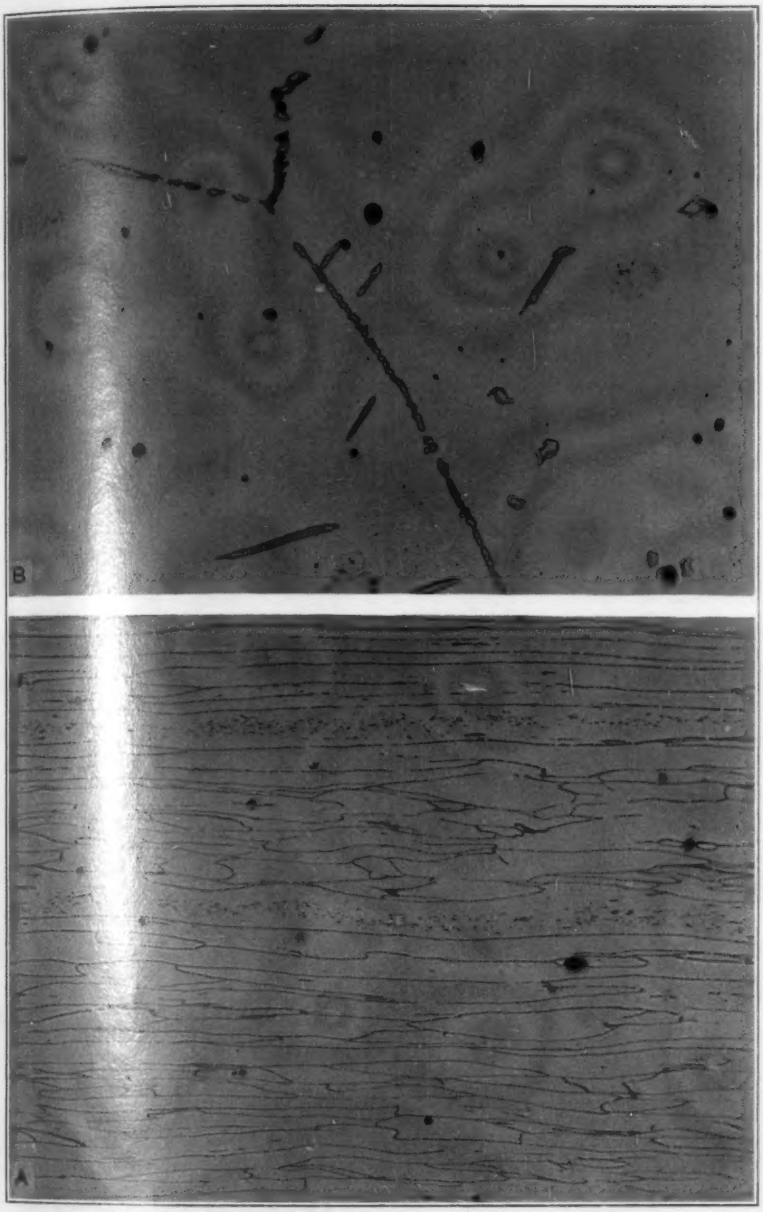

FIGURE 5.—*Microstructure of iron-chromium-aluminum-cobalt alloy (iron 69.0, chromium 23.4, aluminum 5.7, cobalt 1.9, carbon 0.06 percent); × 100.*

A. Sample 1580 (cold-rolled), before heat treatments. *B*. Sample 1580, after heat treatments to various temperatures up to 1,400° C.

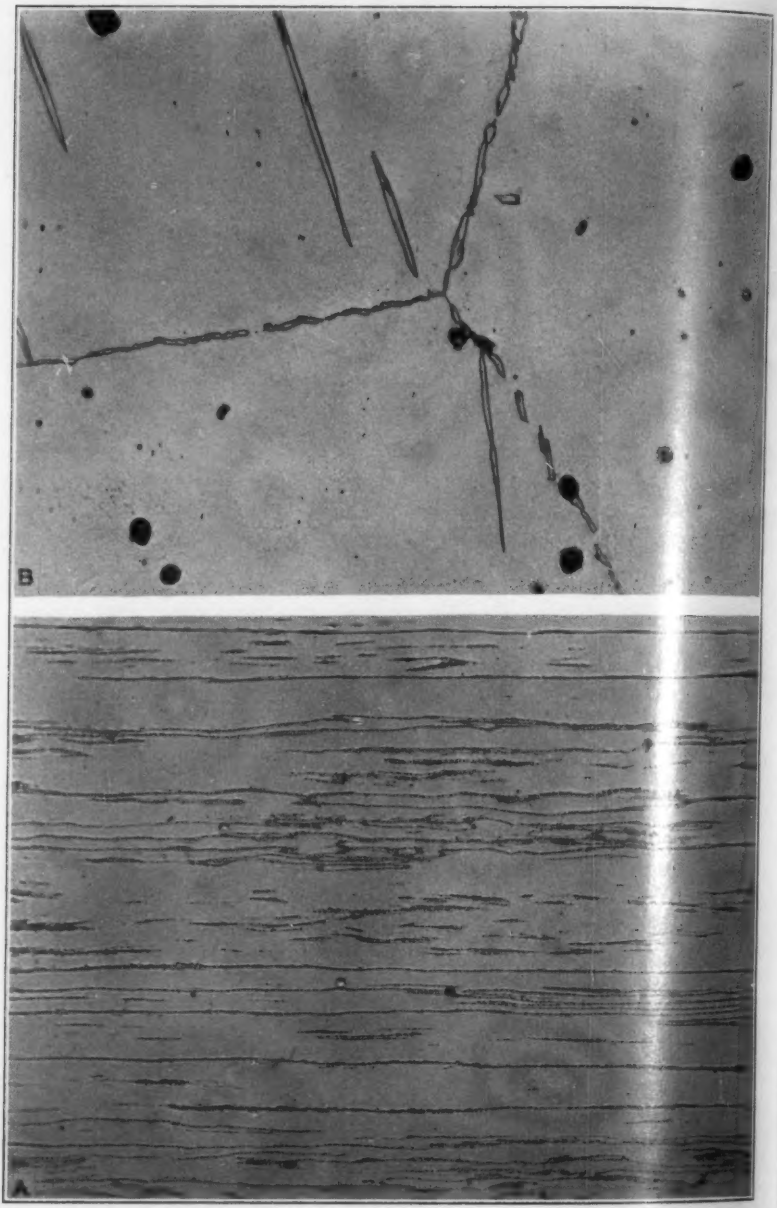

FIGURE 6.—*Microstructure of iron-chromium-aluminum-cobalt alloy (iron 70.9, chromium 22.6, aluminum 4.5, cobalt 2.0, carbon 0.09 percent); ×100.*

A. Sample 1581 (hot-rolled), before heat treatments. *B*. Sample 1581, after heat treatments to various temperatures up to 1,400° C.

3. STRUCTURE

Longitudinal sections were cut from the samples of heat-resisting alloys before the expansion tests and after the heat treatments for the determinations of growth. These sections were prepared for metallographic examination. The sections were etched electrolytically in cold concentrated nitric acid.

Figure 3 shows the structure of iron-chromium-aluminum alloy (sample 1586). Before heat treatments, the hot-rolled alloy consisted of a fairly homogeneous structure of equiaxed crystals with little or no precipitation of intermetallic compounds. After heat treatments to various temperatures up to 1,400° C, excessive grain growth was evident. There still remained in the huge grains the solid solution phase, but with disjointed traces of compounds along the grain boundaries.

Figures 4 to 6 show the structures of iron-chromium-aluminum-cobalt alloys (samples 1579 to 1581). Intermetallic compounds along grain boundaries are exhibited in the micrographs of these alloys before the heat treatments. The constituents were broken up into a series of fine beads in each case, doubtless as a result of severe mechanical working. The effects of this are seen particularly in figures 5 and 6.

The micrographs of the samples of iron-chromium-aluminum-cobalt alloys after heat treatments to various temperatures up to 1,400° C indicate that excessive grain growth occurred. The structures of these alloys after the heat treatments were virtually identical. The micrographs indicate huge grains of a solid solution with abundant precipitation of intermetallic compounds in the grain boundaries and random distribution in small amounts of the same constituent in the form of needles within the grains.

The chief microstructural effect observed as a result of heat treatments on the heat-resisting alloys is in each case a tremendous grain growth.

VI. DISCUSSION

Figure 7 gives a comparison of the expansion curves of heat-treated or hot-rolled heat-resisting alloys, Chromel A [8] and Nichrome IV.[8] Sample 1292 (chromel A) indicates the greatest linear expansion between 20 and 1,000° C, and sample 1581 (iron-chromium-aluminum-cobalt alloy containing the lowest content of aluminum in this group of alloys) indicates the smallest linear expansion. An examination of the thermal-expansion curves in figures 1, 2, and 7, indicates that there is no polymorphic transition in these alloys between 20 and 1,000° C. Öhman [9] stated that Kanthal alloy is ferritic at all temperatures and consequently undergoes no transformation at any temperature.

Referring to the grinding of iron-chromium-aluminum alloy,[9] Hoyt and Scheil [5] stated that this alloy has a low thermal conductivity and a relatively large coefficient of expansion, as a consequence of which relatively large temperature differences must be set up when the metal is ground on the ordinary wheel. On this account the alloy is not ground except under exceptional circumstances or unless the material has been worked to a fine size.

Hoyt [8] stated that in the design and construction of furnaces for operation at the high temperatures which can be attained with the

[8] Data obtained from publication by Hidnert [1].
[9] Smith Alloy No. 10.

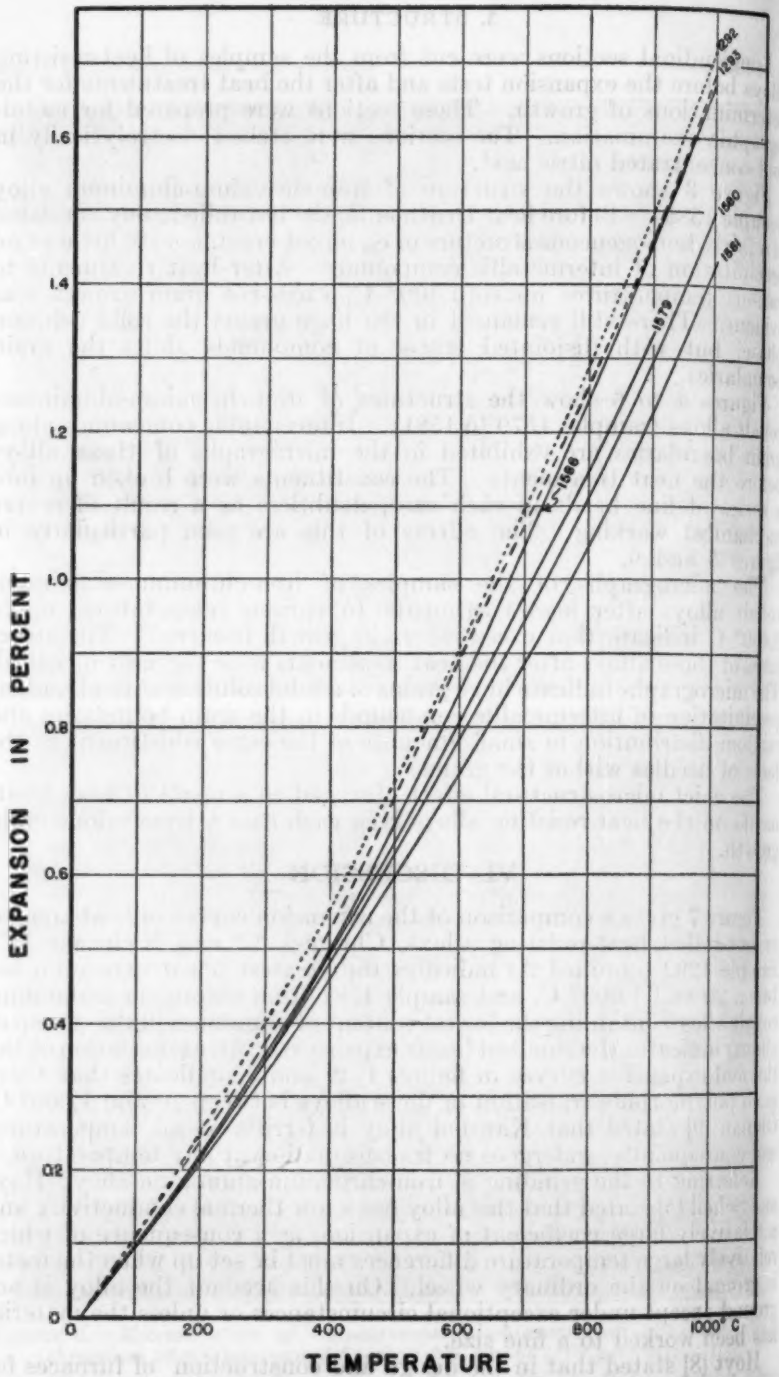

FIGURE 7.—*Comparison of linear expansion of heat-resisting alloys.*

Sample 1586. Iron-chromium-aluminum alloy.
Samples 1579 to 1581. Iron-chromium-aluminum-cobalt alloys.
Sample 1292A. Chromel A.
Sample 1293. Nichrome IV

iron-chromium-aluminum alloy heating element, due regard must be paid to the necessity for providing the right kind of refractories, and for using suitable supports which allow for the thermal expansion, growth, and sagging of the resistance element.

Nordstroem [9] reported that the tensile strength of iron-chromium-aluminum-cobalt alloys falls off sharply on heating. He stated that it is therefore necessary to provide proper support for heating elements made of these alloys. "Corrugated elements hanging from knobs on the sides of the furnace are not suitable above 2,000° F, as the element can elongate by its own weight. The most satisfactory construction is when the element is laid in troughs or shelves formed by protruding ends of header brick."

Ray [10] reported that he had some experience with Kanthal A1 heating-element wire in work which he did with an automatic dental-inlay melting and casting machine. He used about 14 feet of No. 20 or No. 21 gage wire wrapped in small grooves on a cylindrical muffle made of soapstone. Alundum cement and silica firebrick high in free silica were placed in close contact with the wire (in violation of the manufacturer's instructions) to serve as insulation. The muffle was connected so that electric current heated it to about 1,000° C in 3 minutes and then the current was automatically shut off. The muffle was allowed to cool to 300° C, which required about 18 minutes. Intermittent heating and cooling were continued for about 150 hours, after which it was found that the wire had expanded so much that it not only cracked the muffle but also broke the alundum refractory and pushed the porous silica firebrick away. The automatic device which turned on and shut off the current, operated by time and not by temperature. A recording pyrometer indicated that the temperature of the inside of the muffle near the center varied between 1,000 and 1,150° C. The temperature of the heating-element wire was somewhat hotter than this temperature. After 150 hours of operation, which corresponded to more than 400 cycles of heating and cooling, the wire, especially that part near the center, had grown so much that the coils were grouped together. Ray also observed that the resistance of the wire had increased appreciably and consequently a longer time was required to bring the muffle up to 1,150° C at the end of 150 hours than was required at the beginning.

The densities of mechanically worked alloys of iron-chromium-aluminum and iron-chromium-aluminum-cobalt increased 1.12 to 2.50 percent after heat treatments to 1,400° C. Kahlbaum and Sturm [11], Goerens [12], and Johnston and Adams [13] reported smaller increases in density after annealing cold-drawn wires of some metals and alloys. For example, the increase in density for iron after annealing at 1,040° C, was 0.26 percent. The reader is referred to Tammann [14] for a discussion of volume and density changes of metals and alloys.

The samples of heat-resisting alloys indicated excessive growth, excessive density changes, and excessive grain growth as a result of heat treatments at elevated temperatures.

VII. CONCLUSIONS

1. A comparison of the average coefficients of expansion of the two groups of heat-resisting alloys which were investigated, is given in table 7. Coefficients of expansion of Chromel A and Nichrome IV are included in this table.

TABLE 7.—*Comparison of average coefficients of expansion of heat-resisting alloys*

Alloys	Chemical composition					Average coefficients of expansion per degree centigrade									
	Fe	Cr	Al	Co	Ni	20 to 100°C.	20 to 200°C.	20 to 300°C.	20 to 400°C.	20 to 500°C.	20 to 600°C.	20 to 700°C.	20 to 800°C.	20 to 900°C.	20 to 1,000°C.
	%	%	%	%	%	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶
Iron-chromium-aluminum	53.1	38.6	7.9	----	----	11.4 to 12.0	11.9 to 12.2	12.4 to 12.7	12.7 to 13.1	13.2 to 13.9	14.0 to 14.6	14.6 to 15.4	15.0 to 15.9	15.5 to 16.5	16.0 to 17.1
Iron-chromium-aluminum-cobalt	68.5 to 70.9	22.6 to 23.4	4.5 to 6.2	1.9 to 2.0	----	11.4 to 11.7	11.6 to 12.0	11.9 to 12.4	12.1 to 12.9	12.4 to 13.4	12.7 to 13.9	13.0 to 14.4	13.4 to 14.7	13.9 to 15.1	14.5 to 15.8
Chromel A [a]	0.65	19.3	----	----	77.0	13.6	14.0	14.3	14.5	15.1	15.6	16.1	16.5	17.0	17.6
Nichrome IV [b]	.40	20.4	----	----	76.80	13.0	13.3	13.3	13.9	14.7	15.3	15.8	16.2	16.7	17.2

[a] Manganese 2.50 percent.

[b] Manganese 1.92 percent.

2. The average coefficients of expansion of a heat-treated iron-chromium-aluminum alloy containing approximately 53 percent of iron, 39 percent of chromium, and 8 percent of aluminum are slightly greater than the coefficients of a hot-rolled alloy.

3. The substitution of approximately 39 percent of chromium for the same amount of iron in an iron-aluminum alloy containing about 8 percent of aluminum, has little effect on the coefficients of expansion for temperature ranges between 20 and 500° C.

4. The substitution of 4.5 to 6.2 percent of aluminum and about 2 percent of cobalt for an equivalent amount of iron in an iron-chromium alloy containing about 23 percent of chromium, increases the coefficients of expansion.

5. No polymorphic transition was observed in the heat-resisting alloys between 20 and 1,000° C.

6. The heat-resisting alloys indicated growth after various heat treatments at temperatures up to 1,400° C. The growth of the iron-chromium-aluminum-cobalt alloys ranged from 1.21 to 2.81 percent. The growth of the iron-chromium-aluminum alloy was nearly 1 percent. The growth decreased with an increase in the aluminum content. Additional heat treatments on these alloys would probably cause additional growth.

7. The densities of the mechanically worked iron-chromium-aluminum alloy and iron-chromium-aluminum-cobalt alloys increased 1.12 to 2.50 percent as a result of various heat treatments at temperatures up to 1,400° C. The cross-sectional areas of the alloys presumably decreased, for both the densities and the lengths increased.

8. Tremendous grain growth occurred in the iron-chromium-aluminum alloy and iron-chromium-aluminum-cobalt alloys as a result of various heat treatments to elevated temperatures.

The author thanks the following members of the staff of the National Bureau of Standards for the assistance mentioned: J. L. Hague and W. H. Jukkola for the chemical analyses of the heat-resisting alloys; S. Alpher and N. Green for the density determinations; H. O. Willier for the metallographic examination; and J. Burks for his assistance during a part of this investigation.

VIII. REFERENCES

[1] P. Hidnert, *Thermal expansion of heat-resisting alloys: Nickel-chromium, iron-chromium, and nickel-chromium-iron alloys*, BS J. Research **7,** 1031 (1931) RP388.

[2] S. L. Hoyt and R. S. Archer, U. S. Patent 1,995,923 (March 26, 1935) assigned to A. O. Smith Corporation, Milwaukee, Wis.

[3] H. G. A. v. Kantzow, U. S. Patent 1,717,284 (June 11, 1929).

[4] W. Souder and P. Hidnert, *Measurements on the thermal expansion of fused silica*, BS Sci. Pap. **21,** 1 (1926) S524.

[5] S. L. Hoyt and M. A. Scheil, *A new heat-resistant alloy*, Trans. Am. Soc. Metals **23,** 1022 (1935).

[6] A. Schulze, Über die thermische Ausdehnung von Eisenlegierungen, Z. tech. Physik **9,** 338 (1928).

[7] E. Öhman, *High-temperature resistor uses iron-base alloy*, Metal Progress **20,** 78 (Dec. 1931).

[8] S. L. Hoyt, *A new resistor alloy—chromium-aluminum-iron*, Metal Progress **28,** 38 (July 1935).

[9] G. Nordstroem, *Alloys good at temperatures above 2,100° F.*, Metal Progress **28,** 68 (Oct. 1935).
[10] Private communication dated May 10, 1937 from K. W. Ray, Director of Research, General Refineries, Inc., Minneapolis, Minn.
[11] G. W. A. Kahlbaum and E. Sturm, Über die Veränderlichkeit des spezifischen Gewichtes, Z. anorg. Chem. **46,** 217 (1905).
[12] P. Goerens, Über den Einfluss der Wärmebehandlung auf die Eigenschaften von kalt bearbeitetem Flusseisen, Ferrum **10,** 226 (1912).
[13] J. Johnston and L. H. Adams, Die Dichte fester Stoffe, mit besonderer Berücksichtigung der durch hohe Drucke hervorgerufenen dauernden Änderungen, Z. anorg. Chem. **76,** 274 (1912).
[14] G. Tammann, Lehrbuch der Metallkunde, vierte erweiterte Auflage, 1932 (Verlag von Leopold Voss, Leipzig).

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HEATS OF HYDRATION AND TRANSITION OF CALCIUM SULFATE

By Edwin S. Newman and Lansing S. Wells

ABSTRACT

The heats of solution at 25° C in 2.09 molal HCl of gypsum, hemihydrate, natural anhydrite, and anhydrous $CaSO_4$, prepared by heating gypsum at various temperatures, have been determined. From these values the heats evolved in the hydration to gypsum of hemihydrate, and of anhydrite prepared at 1,000° C, were calculated to be 4,100 ±30 and 3,990 ±20 cal/mole, respectively. The heat evolved in the hydration to gypsum of soluble anhydrite prepared by dehydrating gypsum at 75° C is not less than 6,990 cal/mole. In the course of this work X-ray and microscopic studies gave no indication of the existence of more than two forms of anhydrous calcium sulfate: Soluble anhydrite and a modification formed rapidly at high temperatures, the latter being identical with natural anhydrite. The heat evolved in the transition of soluble anhydrite to natural anhydrite is not less than 3,000 cal/mole.

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I. INTRODUCTION

Despite the fact that calcium sulfate and its hydrates have been the subject of many investigations, considerable confusion has existed as to the number of forms and their energy relations. There has also grown up a perplexing terminology. It is universally agreed that gypsum, $CaSO_4.2H_2O$, and natural anhydrite, $CaSO_4$, are distinct compounds. On the other hand, there has been considerable difference of opinion about the anhydrous forms resulting from the dehydration of gypsum and hemihydrate at various temperatures and as to whether or not hemihydrate, $CaSO_4.1/2H_2O$, is a definite compound.

Van't Hoff [1] [1] originated the term "soluble anhydrite" to describe the anhydrous form prepared from gypsum at low temperatures, and

[1] Numbers in brackets refer to literature citations at the end of this paper.

distinguish it from the less soluble anhydrous forms, "dead-burned gypsum" and the naturally occurring anhydrite.

Jung [2], Ramsdell and Partridge [3], and Caspari [4] consider that hemihydrate is a zeolite, basing their conclusions on the fact that X-ray diffraction patterns of the hemihydrate which they secured were identical with those of the products obtained by dehydrating hemihydrate. Thus there arose the term "dehydrated hemihydrate." Feitknecht [5], on the other hand, observed differences in the patterns of hemihydrate and its dehydration product, provided rehydration of the latter was prevented. Onorato [6] and Gallitelli [7] likewise detected differences in the patterns. More recently, Weiser, Milligan, and Ekholm [8, 9], and Posjnak [10] have obtained patterns that leave little doubt that hemihydrate and the anhydrous material resulting from its dehydration at relatively low temperature are different in structure. Since the term "soluble anhydrite" has the advantages of conciseness and prior usage it takes the place in this paper of the more cumbersome "dehydrated hemihydrate" of recent authors to indicate the low-temperature, unstable dehydration product of either gypsum or hemihydrate.

TABLE 1.—*Previously reported heats of hydration to gypsum of* $CaSO_4.1/2H_2O$ *and* $CaSO_4$

Investigator	Literature reference	Heat of hydration to gypsum of $CaSO_4.1/2H_2O$	Method of preparation	Heat of hydration to gypsum of $CaSO_4$	Method of preparation	Method for determining heat of hydration
		cal/mole		cal/mole		
Thomsen	[17]			4,740	Gypsum heated at 120° C.	Direct hydration in calorimeter.
Van't Hoff	[1]	3,921	Gypsum dehydrated in NaCl solution.	4,606	Natural anhydrite.	Application of Clausius-Clapeyron equation to vapor-pressure data.
de Forcrand	[18]	3,860	Gypsum heated to constant weight at 110° C (3 to 4 hr).	5,955	Gypsum heated 4 hr at 155° C.	Heat of solution in water.
				3,220	Above material heated 15 minutes at red heat.	
Mixter	[19]			4,500	Gypsum heated to constant weight at 160 and 200° C.	Heat of fusion with Na_2O_2 and C or S.
Chassevent	[20]	3,800	Gypsum heated in steam at 140° C.	6,570	Gypsum heated at 200° C.	Direct hydration in calorimeter.
Olson	[35]			6,730	Gypsum heated at 140° C.	Direct hydration in calorimeter.
Budnikov	[16]			4,850	Gypsum heated 1 hr at 200° C.	Direct hydration in calorimeter.
				114	Gypsum heated 1 hr at 750° C.	

Certain investigators have suggested the existence of other anhydrous forms of calcium sulfate. LaCroix [11] reported a triclinic modification formed when gypsum was heated slowly to 125° C and a hexagonal form appeared above 255° C. Both of these, he declared, were different from natural anhydrite, to which they changed upon heating to a bright-red heat. Gaubert [12] described three anhydrites, gamma-anhydrite formed below 170° C, beta-anhydrite at about this temperature, and alpha-anhydrite at about 520° C. Jolibois [13]

recognized an active form produced below 350° C and an inactive form above that temperature. Chassevent [14] believed that alpha-$CaSO_4$ existed below and beta-$CaSO_4$ above 300° C, while Grahmann [15] applied the same terms to those forms existing above and below 1,195° C, and reported a melting point of $CaSO_4$ of 1,450° C. Budnikov [16] states that dissociation to CaO and SO_3 begins at 750° C.

Much of the confusion appears to have arisen from failure to attain equilibrium and from acceptance of the properties of a partially converted mixture as those of a new phase. For the same reasons, the thermochemical data also present anomalies which are evident from the values of the heat of hydration listed in table 1.

In the study herein described the energy relations of various forms of calcium sulfate and its hydrates were determined by means of their heats of solution in hydrochloric acid.

II. PREPARATION OF MATERIALS

Gypsum was prepared by two methods: (1) By crystallization from its supersaturated solution (obtained by dissolving hemihydrate in distilled water) and (2) by precipitation from a mixture of approximately equal volumes of 10-percent solutions of reagent quality calcium chloride and sulfuric acid. The preparations were thoroughly washed with distilled water, alcohol, and ether, and the residual ether was allowed to evaporate spontaneously. Seven preparations were made in all. The one finally selected for extended investigation had a loss on ignition of 20.98 percent (theoretical=20.93 percent) and microscopic examination disclosed no foreign material.

The samples of hemihydrate used in this work were prepared by heating 2.000 g of the gypsum, contained in weighed open Pyrex glass capsules, in steam for 3 hours at 115 lb/in.^{2} absolute pressure. The material was next dried in the open capsule approximately 18 hours at 75° C and then allowed to stand exposed to the laboratory air until the heat of solution was determined. Water content as indicated by the loss in weight varied from 6.16 to 6.30 percent (theoretical=6.21 percent). The material had refractive indices corresponding to those reported for hemihydrate [21] and no other material was detected.

Anhydrous calcium sulfate was prepared by heating gypsum in an electric furnace at temperatures ranging from 75 to 1,225° C for times ranging from 5 months to 10 minutes. For the sample prepared at 75° C the gypsum was placed in a vacuum over P_2O_5 to expedite dehydration. At temperatures below 700° C, samples weighing 2.000 g were heated in weighed glass capsules which, immediately after cooling and weighing, were closed with sealing wax and a cover glass. At 700° C and above the gypsum was heated in platinum and kept in tightly corked vials. Approximately 0.2 percent of water (as indicated by loss in weight) remained in the samples prepared at 300° C and below, but at higher temperatures the resulting $CaSO_4$ was anhydrous.

Natural anhydrite, from Midland, Calif., was ground to pass a No. 200 sieve. Determinations of SiO_2, Al_2O_3, Fe_2O_3, and MgO indicated that the total of these materials did not exceed 0.5 percent and the loss on ignition was 1.6 percent. The refractive indices corresponded with those reported [22], and no material other than natural anhydrite was detected microscopically.

III. HEAT-OF-SOLUTION CALORIMETER

1. DESCRIPTION OF CALORIMETER

The calorimeter used was developed at the National Bureau of Standards for determining the heat of solution of cement and is of the type described by Woods [23], Biddle [24], and Stenzel [25]. The calorimeter,[2] shown in figure 1, consists of a reaction vessel, *B*, and an outer watertight jacket, *A*. Chimneys in the jacket lid (only two of which appear in fig. 1) are provided for the thermometer, heater leads, stirrer shaft, and valve stem. The lid, *C*, of the reaction vessel supports a Bakelite sample valve, *D*, and a hollow cylindrical heating unit, *E*, which served also as a stirring tube. All metallic surfaces within the reaction vessel are protected with an acid-resisting vinyl resin lacquer. A clear Bakelite propeller within the stirring tube, driven by a synchronous motor, provides the stirring. The heater is constructed of two close-fitting coaxial cylinders soldered together at the bottom and to the supporting ring at the top. A noninductive resistance of manganin wire is wound in the annular space provided by a recess in the inner cylinder, and the leads are brought out through a channel in the supporting ring and one of the pillars to the corresponding chimney in the jacket. The sample container, *D*, is a hollow cylinder of clear Bakelite closed at the lower end by a mushroom valve of the same material, and at the upper end by a black Bakelite cap supporting the valve stem and spring. The valve stem extends into one of the exit chimneys in the lid of the outer vessel. The outside of the chimney is threaded at the upper end and a threaded bushing bearing against a shoulder on a Bakelite rod, *F*, is screwed down over these threads to open the valve. The sample is placed

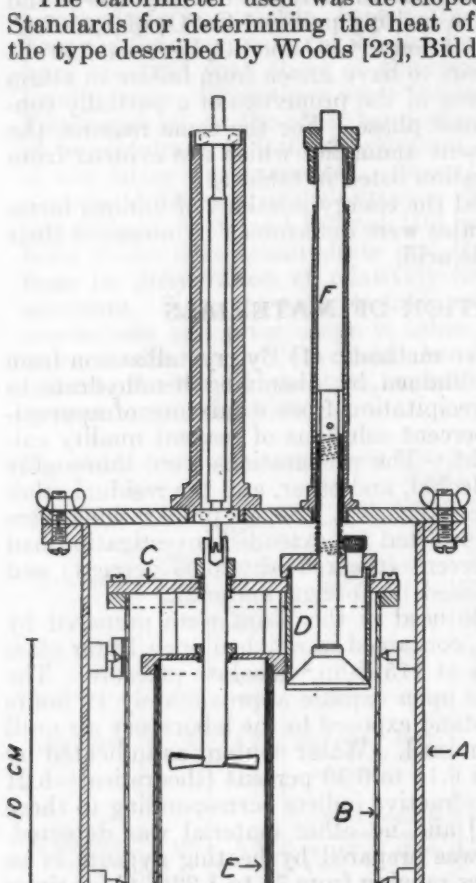

FIGURE 1.—*Heat-of-solution calorimeter.*

A, outer jacket; *B*, reaction vessel; *C*, cover of reaction vessel; *D*, valve for introduction of sample; *E*, heater coil; *F*, rod for opening valve.

[2] Complete details of construction are described in U. S. Bureau of Reclamation Specification 566 for Cement for Boulder Dam.

in the valve cylinder while the calorimeter is being assembled and is introduced into the acid charge by opening the valve after the calorimeter has been placed in the constant-temperature bath and the rate of temperature rise caused by stirring and thermal leakage has reached a constant value. The temperature of the calorimeter is measured with a 25-ohm platinum resistance thermometer incased in a platinum sheath and a Mueller temperature bridge.

The acid charge used in this work was 640.0 g of 2.09 molal [3] hydrochloric acid in water. During a determination the calorimeter was immersed in a water bath controlled automatically at 25.000 ±.005° C. The heat capacity of the calorimeter and contents was measured by introducing a measured amount of electrical energy and measuring the resultant temperature rise. The factor used in converting the international joule to the conventional defined calorie [27] is 4.1833. The heat capacity of the calorimeter and contents and the characteristics of the measuring system were such that on a scale 1.5 m from the galvanometer a deflection of 1 mm was equivalent to 0.26 calorie. Deflections were estimated to 0.25 mm, equivalent to 0.00001 ohm or 0.0001° C. Changes in resistance of 0.0001 ohm (equivalent to 0.001° C) could be read directly on the bridge dials. The resistance-temperature coefficient of the thermometer was 0.1010 at 25° C, the temperature of the experiments. The calorimeter samples were of such size that they contained anhydrous $CaSO_4$ equivalent to 2.000 g of $CaSO_4.2H_2O$. Samples of precipitated gypsum, natural anhydrite, and anhydrous $CaSO_4$ prepared at temperatures of 700° C and above were introduced by means of the Bakelite valve; those of hemihydrate and anhydrous $CaSO_4$ prepared below 700° C, by removing the valve, substituting the capsule, and crushing it against the bottom of the calorimeter.

2. CALCULATIONS

The temperature changes observed in the calorimetric determinations were corrected by the "Second Geophysical Laboratory Formula" given by White [26].

The percentage "energy equivalent error" [27], a, of the heat-capacity measurements of the calorimeter was calculated by the formula

$$a = \pm (100)\frac{2\sqrt{\sum v^2/m(m-1)}}{\text{(value of energy equivalent)}},$$

in which $\sum v^2$ is the sum of the squares of the deviations from the arithmetical mean of m experimental values.

Likewise, the percentage "reaction error", b, was calculated by the formula

$$b = \pm (100)\frac{2\sqrt{\sum v^2/n(n-1)}}{\text{(value of reaction energy)}},$$

in which n is the number of determinations of the heat of solution.

The final assigned "precision error" [4] of the average value for the heat of solution is

$$\text{"precision error"} = \pm\sqrt{a^2+b^2}.$$

[3] A molal solution is one containing 1 gram-molecule of solute per 1,000 g of solvent.
[4] The energy equivalent error of the heat capacity was ±0.034 percent.

The last equation is also used to calculate the error of the sum or difference of two heats of solution A and B affected with errors a and b, but the errors in this case must be expressed in calories and not in percentages.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

1. HEATS OF SOLUTION

The average of 21 determinations of the heat of solution of five preparations of gypsum was -33.01 cal/g ± 0.20 percent. This value, equivalent to $-5{,}678$ cal/mole, was used in calculations of the heats of hydration. A sample of gypsum prepared from $CaCl_2$ and H_2SO_4 was used for a study of the heat of solution of the products resulting from heating gypsum at different temperatures for varying lengths of time. Table 2 contains data pertaining to this preparation. The average of five determinations of the heat of solution of this sample was -33.06 cal/g ± 0.36 percent (column 2). Column 3 shows the data pertaining to the hemihydrate, column 4 those of the material resulting from heating the gypsum at 75° C, and columns 5 and 6 those of the materials heated at 900 and 1,000° C, respectively. The table also contains the results of six determinations of the heat of solution of natural anhydrite (column 7).

TABLE 2.—*Heats evolved in the solution of calcium sulfate and its hydrates in 2.09 molal aqueous* HCl *at 25° C*[a]

Determination number	$CaSO_4.2H_2O$	$CaSO_4.1/2\ H_2O$	$CaSO_4$[b]	$CaSO_4$[c]	$CaSO_4$[d]	Natural anhydrite
1	2	3	4	5	6	7
	cal/g	cal/g	cal/g	cal/g	cal/g	cal/g
1	−33.17	−11.20	+9.27	−12.30	−12.80	−12.35
2	−33.20	−10.70	+9.52	−12.38	−12.85	−11.90
3	−32.92	−11.00	+9.42	−12.63	−12.80	−12.80
4	−32.92	−11.11	+9.42	−12.37	−12.54	−12.23
5	−33.07	−11.36		−12.43	−12.75	−13.05
6		−10.97		−12.43		−12.21
7		−11.04		−12.52		
Average	−33.06 ±.36%	−11.05 ±1.4%	+9.41 ±1.2%	−12.44 ±1.9%	−12.75 ±0.86%	−12.43 ±2.8%

[a] The ratio of moles of $CaSO_4$ to HCl was 1 to 107.
[b] Heated at 75° C over P_2O_5.
[c] Heated at 900° C.
[d] Heated at 1,000° C.

The average heat of solution of the anhydrous calcium sulfate prepared at 75° C was $+9.41$ cal/g. It should be noted from figure 2, which shows the data obtained with the $CaSO_4$ prepared from this sample of gypsum, that there was very little change, with time of heating, in the heat of solution of the product prepared at this temperature.

It is obvious from figure 2 that samples of $CaSO_4$ prepared by heating the gypsum at different intermediate temperatures for appropriate lengths of time may have identical heats of solution.

For example, a sample heated for 10 minutes at 500° C had the same heat of solution as one heated 110 hours at 400° C. This condition has often been overlooked and undoubtedly has led to some of the confusion about the energy relations of the different forms.

The $CaSO_4$ prepared at higher temperatures gave heats of solution less than +9.41 cal/g. Furthermore, the heat of solution decreased with increased time of heating, until, at a temperature of 900° C, there was again very little change in the heat of solution with the time of heating. The $CaSO_4$ prepared at 1,000° C also showed little or no change with the time of heating, although the heat of solution was slightly more negative (0.31 cal/g) than the average value obtained with material heated at 900° C (see table 2). Although this suggests that a product having a still more negative heat of solution might be obtained at a still higher temperature, nevertheless, this is doubtful

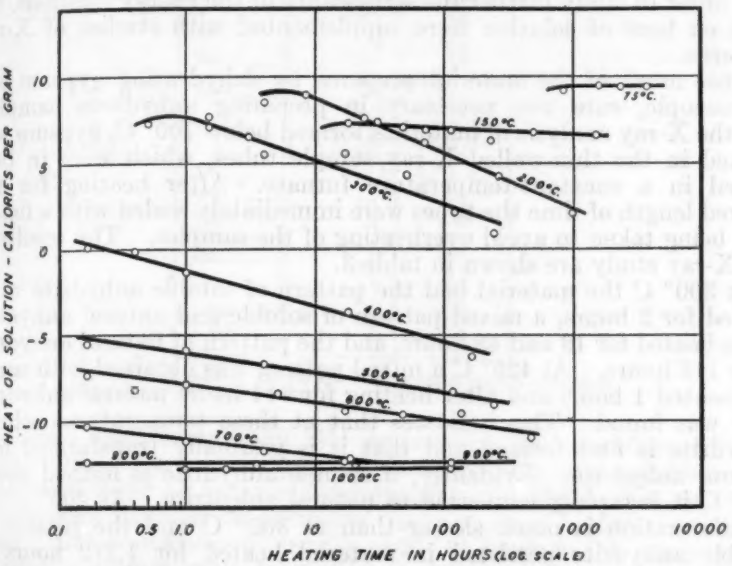

FIGURE 2.—*Relation of heat of solution of anhydrous* $CaSO_4$ *in 2.09 molal* HCl *at 25° C to the time and temperature of heating.*

because of the dissociation which will occur at higher temperatures. Marchal [28] has determined the dissociation pressure of $CaSO_4$ at 1,000, 1,100, and 1,230° C and found it to be 8, 24, and 97 mm of Hg, respectively. Since the heat of solution of 1.5 g of CaO in 640 g of 2.09 molal HCl in this calorimeter is +834 cal/g [29], it is evident that any dissociation of $CaSO_4$ will result in an increase in the heat of solution. Gypsum heated at 1,100° C for 1, 4, and 19 hours gave heats of solution of −11.0, +4.5, and +225 cal/g, respectively. The corresponding free CaO[5] determinations gave 0.1, 1.1, and 20.8 percent, respectively.

It is evident, from the foregoing, that no significant decrease in the heat of solution of gypsum heated to temperatures above 1,000° C can be directly determined by the method employed, because of the increasing amounts of free lime formed at higher temperatures. Consequently, the value −12.67 cal/g ±0.66 percent, the average of 19 determinations of the heat of solution of the material prepared by heating eight different preparations (including selenite, a naturally

[5] Free lime was determined by titration with *N*/10 H_2SO_4 and phenolphthalein. One-gram samples were placed in Erlenmeyer flasks with 50 ml of H_2O and boiled. Titration was considered complete when no return of color occurred with 30 minutes' boiling after the final addition of acid.

occurring form) of gypsum at 1,000° C for times ranging from 1 to 110 hours, was chosen to calculate the heat of hydration of the high temperature modification of $CaSO_4$.

In view of the fact that the heat of solution of the natural anhydrite (see table 2) would be made slightly less negative by the presence of impurities having an exothermic heat of solution in HCl, the values −12.67 cal/g for the high temperature modification and −12.43 cal/g for the natural anhydrite are considered to be in agreement.

2. X-RAY DIFFRACTION PATTERNS

In order to study further the significance of the energy relations, the data on heat of solution were supplemented with studies of X-ray patterns.

Since much of the material prepared by dehydrating gypsum was hygroscopic, care was necessary in preparing anhydrous samples. For the X-ray analysis of materials formed below 700° C, gypsum was packed in the thin-walled X-ray sample tubes, which were in turn placed in a constant-temperature furnace. After heating for the desired length of time the tubes were immediately sealed with a flame, care being taken to avoid overheating of the samples. The results of the X-ray study are shown in table 3.

At 300° C the material had the pattern of soluble anhydrite when heated for 2 hours, a mixed pattern of soluble and natural anhydrite when heated for 19 and 48 hours, and the pattern of natural anhydrite after 115 hours. At 425° C a mixed pattern was obtained with material heated 1 hour, and after heating for 114 hours natural anhydrite only was found. This indicates that at these temperatures soluble anhydrite is first formed and that it is gradually transformed into natural anhydrite. Evidently, if soluble anhydrite is formed above 425° C it is rapidly converted to natural anhydrite. At 200° C the transformation is much slower than at 300° C and the pattern of soluble anhydrite persisted in material heated for 1,272 hours at 200° C. At temperatures below 200° C the conversion appears to be very slow. Budnikov [30] obtained natural anhydrite by dehydrating gypsum over P_2O_5 under reduced pressure at 40° C but not until a year and a half had passed. That the transformation of gypsum to natural anhydrite is accelerated at low temperatures by water is indicated by the data for 170 and 210° C in table 3

The heats of solution of samples heated at 75 and 150° C (fig. 2) indicate but little change in the energy content with time of heating. At 200, 300, and 400° C the decrease in the heat of solution might at first thought be attributed entirely to the transformation from the soluble to the natural anhydrite, were it not for the fact that at the end of 115 hours at 300° C the heat of solution of the product which the X-ray pattern indicated solely as natural anhydrite was about 14 cal/g greater than that of the natural anhydrite (or the $CaSO_4$ heated at 900° C). Notwithstanding the decreases in the heat of solution of the products prepared at temperatures of 500° C and above, there was no change in the X-ray patterns, all of which corresponded to that of natural anhydrite. From data on heats of solution alone it would appear that the soluble anhydrite content of the samples should be from 10 to 65 percent, corresponding with heats of solution of −10 and +2 cal/g, respectively. It seems certain that the presence of such quantities of soluble anhydrite would be registered in the

X-ray pattern, and it is difficult therefore to believe that the change in heat of solution is entirely accounted for by the transition from soluble to natural anhydrite.

TABLE 3.—*X-ray diffraction patterns of* $CaSO_4$ *heated at constant temperature*

Temperature	Time of heating	Pattern [a]
° C	*Hours*	
110	3,670	*SA*
150	170	*SA*
	624	*SA*
	2,060	*SA*
170 [b]	1½	*NA*
200	3	*SA*
	145	*SA*
	670	*SA & NA*
210 [b]	44	*NA*
300	2	*SA*
	19	*SA & NA*
	48	*SA & NA*
	115	*NA*
400	½	*SA & NA*
425	1	*SA & NA*
	114	*NA*
450	1	*NA*
500	½	*NA*
625	1	*NA*
	114	*NA*
900	1	*NA*
	114	*NA*
1,100	4	*NA*
1,225	2	*NA*

[a] *SA* indicates soluble anhydrite; *NA* indicates natural anhydrite.
[b] Heated in contact with water.

Laschenko and Kompanskii [31] determined the densities of the products formed by heating gypsum, hemihydrate, and soluble anhydrite for 1 hour at various temperatures and found that as the materials were exposed to increased temperatures higher densities resulted. Determinations of density at 25° C, made in this investigation, using picnometers and butyl alcohol, gave values ranging between 2.70 and 2.94 g/cm^3 which increased both with the time of heating and with the temperature at which the material had been heated. Since no shifts were observed in the lines of the X-ray patterns such as would accompany [32] the density changes indicated, it is felt that too much significance should not be placed on the density values obtained, especially in view of the well-known difficulties of determining accurately the density of powdered material.

The breadth of the lines in a powder X-ray pattern is a function of the constants of the apparatus and of the size of the particles in the sample. Above a certain limit an increase in particle size has little effect upon the breadth until a size is reached so large that all possible orientations are no longer present in the sample; below this limit an increase in particle size results in a gradual narrowing of the originally diffuse reflections into lines. Although there appeared to be an increase in the size of the particles upon heating (as will be mentioned particularly for material heated at 900° C) the fact that the X-ray patterns did not show this effect on the breadth of the lines may be explained on the basis either that there was not an appreciable quantity of sufficiently small material, or that there actually was little or no increase in the size of such of that material as may have been present.

3. MICROSCOPIC EXAMINATION

Microscopic examination showed that after heating the samples, nearly all of the calcium sulfate samples were composed of extremely small crystals (0.5 to 2.0 microns in diameter) possessing random orientation in aggregates having the shape of the original gypsum particles. These crystals were so small that their optical properties, other than an approximate mean refractive index, could not be determined. In general, the refractive index was raised by heating.

A sample maintained at 900° C for 5 days was, however, composed of medium sized (5 to 10 microns in diameter) tabular crystals, the optical character and refractive indices of which agreed with those of natural anhydrite. The increase in crystal size suggests that perhaps a similar change occurs at lower temperatures, even though not reflected in the X-ray patterns. Fricke, Schnabel, and Beck [33] found a maximum change in heat of solution in HCl of $Mg(OH)_2$ of 850 cal/mole, which they attributed to surface changes. This corresponds to approximately 14 cal/g, or very nearly the same as the maximum change that in this work cannot be ascribed satisfactorily to a change in the content of soluble anhydrite of a sample of $CaSO_4$. It seems probable that surface change caused by crystal growth contributes to the change in heat of solution of anhydrous $CaSO_4$, although from present data its effect cannot be disentangled from that of the change in soluble anhydrite content.

4. HEAT OF HYDRATION AND TRANSITION

The heats of hydration of the various forms of calcium sulfate may be calculated from the heats of solution. To do so, however, it is necessary to know the heat effect of the water of crystallization of the hydrates. Interpolation of Rossini's data [34] for hydrochloric acid gives the value 17 cal/mole for the partial molal heat content of water in 2.09 molal HCl. This represents the heat effect of adding water to the hydrochloric acid solution, provided that no dilution occurs, a condition approximated when the 0.42 g of water of crystallization contained in the gypsum sample is added to 640 g of acid solution. When 0.42-g samples of water were used as the calorimeter sample the values 14 and 19 cal/mole were obtained. These agree as well as could be expected with Rossini's value, which was used in the calculations.

The following thermochemical equations may be written, using the heats of solution. The values given are those of ΔH, the increment in the heat content, that is, the minus sign indicates evolution of heat. In all cases where the expression "soln" appears, the aqueous solution 0.017 molal $CaSO_4$ and 2.09 molal HCl is indicated. Thus, from the data on the heat of solution, the heat of hydration of hemihydrate to gypsum becomes:

$CaSO_4.1/2H_2O(c) = CaSO_4(soln) + 1/2H_2O(soln)$,	$\Delta H = +1{,}604 \pm 25$ cal
$CaSO_4(soln) + 2H_2O(soln) = CaSO_4.2H_2O(c)$,	$\Delta H = -5{,}678 \pm 11$
$1\frac{1}{2}H_2O(liq) = 1\frac{1}{2}H_2O(soln)$,	$\Delta H = -25$
$CaSO_4.1/2H_2O(c) + 1\frac{1}{2}\ H_2O(liq) = CaSO_4.2H_2O(c)$,	$\Delta H = -4{,}099 \pm 27$ cal.

Similarly, the values $\Delta H = -6{,}991 \pm 19$ and $\Delta H = -3{,}989 \pm 16$ calories per mole are found for the heat of hydration to gypsum of $CaSO_4$ prepared at 75 and 1,000° C, respectively. From the values

of the heats of solution the heat of transition of soluble anhydrite to natural anhydrite is calculated to be $\Delta H = -3{,}002 \pm 22$ cal/mole.

It is felt that rounding the results to the nearest 10 cal gives values that are reasonably certain.

It is likely that the transition from the unstable or soluble anhydrite prepared in this investigation to the stable or natural anhydrite begins as soon as there is any of the unstable modification formed, and that it proceeds simultaneously with the continued dehydration of the remaining hydrated material. If such is the case, soluble anhydrous calcium sulfate is a mixture of the stable and unstable forms and the energy level corresponding to the pure unstable form is never reached. The highest heat of solution obtained is, consequently, to be considered lower than the true value since it is entirely possible that if the pure substance were prepared it would have an appreciably higher heat of solution. Hence, the heats of hydration and transition of soluble anhydrite presented here are to be considered minimum rather than the real values.

When gypsum having a heat of solution of -33.06 cal/g is heated it loses water with the formation of hemihydrate, the heat of solution of which is -11.05 cal/g. The hemihydrate on further heating will be converted to soluble anhydrite with a positive heat of solution ($+9.41$ or more cal/g) and this in turn will be transformed to natural anhydrite having a negative heat of solution, -12.67 cal/g. Since hemihydrate and soluble anhydrite are unstable intermediate products in the transformation of gypsum to natural anhydrite, the relative amounts of these constituents in the heated material will depend largely upon the temperature and time of heating. Even before the hemihydrate has been completely transformed to soluble anhydrite the transformation of soluble anhydrite to natural anhydrite may be well under way. The variable and low results of previous investigators can be partially explained by assuming that the material they used contained variable amounts of the stable and unstable anhydrites and, further, by either or both the length of time required to complete direct hydration or solution (in water) in the calorimeter and the accuracy of measurement of temperature differences. It seems then, that the earlier determinations of the heat of hydration of the forms of calcium sulfate were performed under handicaps to which the present investigation was not subject and that the values here presented may be considered reliable.

V. SUMMARY

The heats evolved in the hydration to $CaSO_4.2H_2O$ at 25° C of $CaSO_4.1/2H_2O$ prepared by treating gypsum with steam in the autoclave, and of $CaSO_4$ prepared by heating gypsum at 1,000° C, have been determined and found to be $4{,}100 \pm 30$ and $3{,}900 \pm 20$ cal/mole, respectively. The heat evolved in the hydration to $CaSO_4.2H_2O$ of soluble anhydrite prepared by dehydrating gypsum at 75° C is not less than 6,990 cal/mole. During the progress of this work no indications were found of more than two anhydrous forms of calcium sulfate; soluble anhydrite, and a modification formed rapidly at high temperatures, the latter being identical with natural anhydrite. The heat evolved in the transition of soluble anhydrite to natural anhydrite is not less than 3,000 cal/mole.

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VI. REFERENCES

[1] Van't Hoff, et al., Z. physik. Chem. **45,** 257 (1903).
[2] Jung, Z. anorg. allgem. Chem. **142,** 73 (1925).
[3] Ramsdell and Partridge, Am. Mineral. **14,** 59 (1929).
[4] Caspari, (a) Nature **133,** 648 (1934); (b) Proc. Roy. Soc. (London) [4] **155,** 41 (1936).
[5] Feitknecht, Helv. Chim. Acta **14,** 85 (1931).
[6] Onorato, Periodico Mineral. **3,** 138 (1932).
[7] Gallitelli, Periodico Mineral. **4,** 1, 132 (1933).
[8] Weiser, Milligan, and Ekholm, J. Amer. Chem. Soc. **58,** 1261 (1936).
[9] Weiser and Milligan, J. Amer. Chem. Soc. **59,** 1457 (1937).
[10] E. Posjnak, Private communication.
[11] LaCroix, Compt. rend. **126,** 360, 553 (1898).
[12] Gaubert, Bul. soc. franç. minéral. **57,** 252 (1934).
[13] Jolibois, Bul. soc. chim. **41,** 117 (1927).
[14] Chassevent, Ann. chim. **7,** 43 (1927).
[15] Grahmann, Z. anorg. Chem. **81,** 257 (1913).
[16] Budnikov and Gulinova, Ann. secteur anal. phys.-chim. Inst. chim. gén. (USSR) **8,** 357 (1936).
[17] Thomsen, Thermochemische Untersuchungen, **III,** 249 (Barth, Leipzig, 1886).
[18] de Forcrand, Bul. soc. chim. **35,** 781 (1906).
[19] Mixter, Am. J. Sci. **40,** 23 (1915).
[20] Chassevent, Compt. rend. **179,** 44 (1924).
[21] Winchell, The Microscopic Characters of Artificial Minerals, p. 226. (John Wiley & Sons, London, 1931).
[22] Larsen and Berman, The Microscopic Determination of the Nonopaque Minerals. Bul. 848, U. S. Geological Survey (1934).
[23] Woods, Steinour, and Starke, Ind. Eng. Chem. **24,** 1207 (1932).
[24] Biddle and Kelly, Proc. Am. Soc. Testing Materials **33,** pt. II, 571 (1933).
[25] Stenzel and Morris, Ind. Eng. Chem., Anal. Ed. **6,** 246 (1934).
[26] White, The Modern Calorimeter, p. 42 (The Chemical Catalog Co., New York, N. Y., 1928).
[27] Rossini, Chem. Rev. **18,** 233 (1936).
[28] Marchal, J. chim. phys. **23,** 38 (1926).
[29] Wells and Taylor, J. Research NBS **19,** 215 (1937) RP1022.
[30] Budnikov, Z. anorg. allgem. Chem. **157,** 87, (1927).
[31] Laschenko and Kompanskii, J. Russ. Phys. Chem. Soc. **60,** 579 (1928).
[32] Burger, Physica **2,** 114 (1922).
[33] Fricke, Schnabel, and Beck, Z. Elektrochem. **42,** 881 (1936).
[34] Rossini, BS J. Research **9,** 679 (1932) RP499.
[35] Olson, Compt. rend, **179,** 1041 (1924).

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REPRODUCIBILITY OF THE SILVER-SILVER CHLORIDE ELECTRODE

By Edgar Reynolds Smith and John Keenan Taylor

ABSTRACT

A study was made of the reproducibility of the electrolytic, thermal-electrolytic, and thermal types of the silver-silver chloride electrode in 0.05 *N* solution of potassium chloride. The presence or absence of light, and of air dissolved in the solution, have no significant effect on their potentials. A marked aging effect was noted, the origin of which was traced to concentration-polarization occurring during the preparation of the electrodes. The attainment of concentration equilibrium between freshly prepared electrodes and solution is slow and may require from 1 to 20 days, depending on porosity of the electrodes and stirring of the solution. For the same reason, freshly prepared electrodes behave as cathodes towards aged electrodes, the initial difference in potential often exceeding a millivolt. When sufficient time is allowed for the establishment of concentration equilibrium, these types of silver-silver chloride electrodes assume the same potential, within about 0.02 mv.

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I. INTRODUCTION

In addition to its individual importance, the silver-silver chloride electrode is finding increasing use as a secondary reference electrode to replace the calomel half-cell.[1] Many important reactions occur in chloride solutions, where this electrode can be applied directly with convenience, because of its compact solid form. Thus by its use, liquid junctions, generally a source of uncertainty in otherwise precise measurements, can often be avoided.

Among the various types of the silver-silver chloride electrode that have been proposed, there are three whose convenience of form and ease of preparation have led to their popular adoption. These particular types are electrolytic, thermal-electrolytic, and thermal. The electrolytic type [2] is made by electroplating silver on a base of platinum and then forming a coating of chloride on the silver by electrolysis in a chloride solution. The platinum base may be in the form of gauze, foil, or wire. The thermal-electrolytic type [3] is

[1] B. Wingfield, W. H. Goss, W. J. Hamer, and S. F. Acree, ASTM Bul. **90**, 15 (1938). W. J. Hamer, Trans. Electrochem. Soc. **72**, 63 (1937). C. N. Murray and S. F. Acree, BS J. Research **7**, 713 (1931) RP369.

[2] H. Jahn, Z. physik. Chem. **33**, 545 (1900). D. A. MacInnes and K. Parker, J. Am. Chem. Soc. **37**, 1445 (1915). D. A. MacInnes and J. A. Beattie, J. Am. Chem. Soc. **42**, 1117 (1920). A. S. Brown, J. Am. Chem. Soc. **56**, 646 (1934). A. S. Brown and D. A. MacInnes, J. Am. Chem. Soc. **57**, 1356 (1935). T. Shedlovsky and D. A. MacInnes, J. Am. Chem. Soc. **58**, 1970 (1936).

[3] G. N. Lewis, J. Am. Chem. Soc. **28**, 158 (1906). A. A. Noyes and J. H. Ellis, J. Am. Chem. Soc. **39**, 2532 (1917). H. S. Harned, J. Am. Chem. Soc. **51**, 416 (1929).

prepared by heating a paste of silver oxide and water, supported on a small spiral of platinum wire, in an electric furnace at 400° C to convert the silver oxide to a porous globule of silver, and then electrolytically coating the silver with chloride. The thermal type[4] is made by heating to decomposition in an electric furnace a paste of silver chlorate, silver oxide, and water, supported on a small spiral of platinum wire. By this method of preparation, an intimate mixture of silver and silver chloride is formed on the supporting wire by one thermal operation, without resort to electrolysis.

An examination of the literature reveals conflicting opinions and data concerning the reproducibility and constancy of the silver-silver chloride electrode.[5] In this investigation a number of electrodes of the electrolytic, thermal-electrolytic, and thermal types were prepared and tested for reproducibility and constancy in the presence and absence of light, and in the presence and absence of dissolved air. Each type was tested first separately by intercomparing electrodes of the same kind and then, after conditions of reproducibility and constancy were established, the different types were compared to determine what differences might exist between the final equilibrium values of potential of each type.

II. APPARATUS AND MATERIALS

The measurements of electromotive force were made with a Rubicon, type B, high-precision potentiometer and an unsaturated Weston standard cell, both of which were calibrated by the Electrical Division of this Bureau. The galvanometer had a sensitivity of 0.15 mm per microvolt when measuring the electrodes.

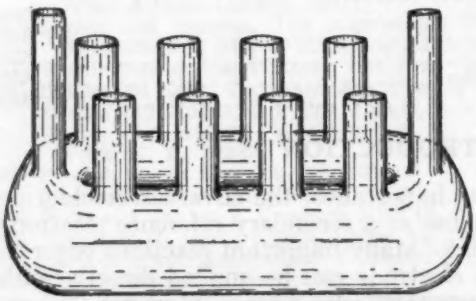

FIGURE 1.—*Cell for comparing electrodes in air-saturated solutions with or without exclusion of light.*

For the intercomparison of electrodes in air-saturated solution, two cells of the type shown in figure 1 were used. Each of these cells had a volume of 400 ml and held 8 electrodes. For measurements in the absence of light, one of these was coated with black casein paint which is water-soluble but impervious to the oil of the thermostat. Another type of cell, shown in figure 2, was used to intercompare electrodes in the absence of oxygen. These cells were made from 400-ml dye beakers. A gas-bubbling jet was sealed into each, as shown in the figure, and the top was closed by a large rubber stopper through which were inserted the electrodes and a gas exit tube. To remove oxygen from the solution in these cells, nitrogen, freed from oxygen by passage through pyrogallol solution, followed by passage through a solution of the same composition as that in the cell, was bubbled through the cells.

The cells were immersed in an oil bath of 80 liters capacity, equipped with a stirrer, heater, cooling coil, and a thermoregulator. Since the

[4] C. K. Rule and V. K. La Mer, J. Am. Chem. Soc. **58**, 2339 (1936).

[5] A. A. Noyes and J. H. Ellis, J. Am. Chem. Soc. **39**, 2532 (1917). M. Randall and L. E. Young, J. Am. Chem. Soc. **50**, 989 (1928). E. R. Smith, BS J. Research **2**, 1140 (1929) RP74. W. R. Carmody, J. Am. Chem Soc. **51**, 2901 (1929); **54**, 188 (1932). A. S. Afanasiev, J. Am. Chem. Soc. **52**, 3477 (1930).

measurements to be made were of differences in potential of silver-silver chloride electrodes having practically the same temperature coefficients of electromotive force, only a uniform temperature was maintained in the bath, no effort being made to secure any precisely fixed temperature. The observations reported in this paper are for room temperatures, which were within the range of 25 to 30° C.

The leads from the cells to the potentiometer were insulated enameled copper wires supported on Bakelite insulators. To shield the electrical system, all parts, including the thermostat and the cells, rested on, or had metal supporting bases connected to copper sheeting at uniform potential.[6]

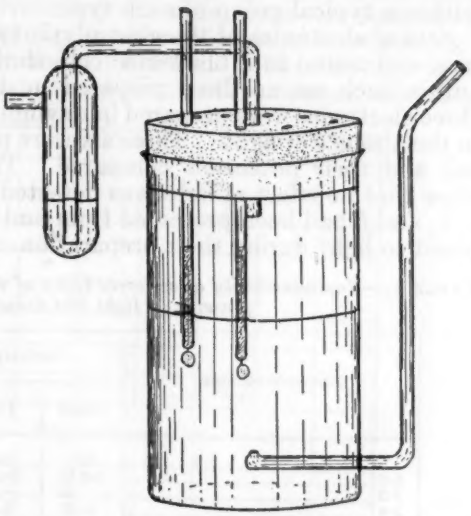

FIGURE 2.—*Cell for comparing electrodes in oxygen-free solutions with or without exclusion of light.*

The chemicals used were of reagent grade, tested and found to conform to specifications adopted by the American Chemical Society.[7] The potassium and sodium chlorides were further purified by recrystallization. Silver chlorate was prepared from silver oxide and chloric acid, and was recrystallized three times. Silver oxide was prepared by adding sodium hydroxide solution to a slight excess of silver nitrate and thoroughly washing the resulting precipitate. The silver-plating solution was prepared and used essentially according to the procedure given by Brown.[8]

III. REPRODUCIBILITY OF THE ELECTRODES

Silver-silver chloride electrodes of the electrolytic type were made by welding rectangular pieces of platinum gauze, 0.5 by 1 cm, to platinum wires which then were sealed into the ends of 6-cm lengths of soft glass tubing. These platinum bases were cleaned by heating to brightness in a flame and then immersing them in boiling concentrated nitric acid. They were next electroplated with silver at a current of 4 ma per electrode for 24 hours. After removal from the plating bath, they were washed in frequent changes of distilled water for a period of 10 days to remove adsorbed contaminations.[9] After the washing, they were chloridized by connecting them in series as anodes in molar hydrochloric acid and passing a current of 4 to 6 ma for 1 hour. Before transferring to the cell for measurement, they were washed first in distilled water and finally in a solution of the same composition as that in the cell. Five sets of these electrodes, having eight in each set, immersed in 0.05-*N* potassium chloride in the

[6] W. P. White, J. Am. Chem. Soc. **36**, 2011 (1914).
[7] Ind. Eng. Chem. **17**, 756 (1925); **18**, 759 (1926).
[8] A. S. Brown, J. Am. Chem. Soc. **56**, 646 (1934).
[9] W. R. Carmody, J. Am. Chem. Soc. **51**, 2901 (1929).

presence of light and dissolved air, showed an average reproducibility of 0.02 mv within each set made at the same time. A few other sets with platinum-foil and platinum-wire bases exhibited the same degree of reproducibility. Under the same conditions, several groups of thermal-electrolytic and thermal electrodes agreed within each group with an average deviation of about 0.02 mv. These results are summarized in table 1, where data are given of differences in potential within a typical group of each type.

Sets of electrodes of the electrolytic type, chloridized in total darkness and tested in a blackened cell, showed the same reproducibility within each set as those prepared in daylight. In one experiment three electrodes were prepared in daylight and, at the same time, three in the absence of light. These six were placed together in a blackened cell and their potentials compared. The results, given in table 2, show that no effect of light was detected. In table 2, electrodes Nos. 1, 3, and 5 had been protected from and Nos. 2, 4, and 6 had been exposed to light during their preparation.

TABLE 1.—*Reproducibility of different types of silver-silver chloride electrodes in the presence of light and dissolved air*

Electrode number	Electrolytic type			Thermal-electrolytic type	Thermal type
	Gauze	Foil	Wire		
	mv	mv	mv	mv	mv
1–2	+0.04	+0.02	−0.02	−0.03	−0.04
1–3	.00	−.01	−.02	+.01	+.01
1–4	+.01	+.02	−.02	−.03	.00
1–5	+.01	+.02	−.01	+.02	−.03
1–6	+.02	+.01	−.03	−.03	−.03
1–7	+.03	−.01	−.04	−.04	−.05
1–8	+.01	−.01	−.01	.00	.00
Average deviation	0.02	0.02	0.02	0.02	0.02

TABLE 2.—*Comparison of electrodes, prepared in the presence and absence of light, in air-saturated solution*

Electrode number [a]	Potential difference
	mv
1–2	+0.01
1–3	+.01
1–4	−.02
1–5	−.02
1–6	+.02

[a] Electrodes 1, 3, and 5 protected from light; 2, 4, and 6 exposed to light.

IV. CHANGE IN POTENTIAL WITH AGE

The results cited in the previous section show that when silver-silver chloride electrodes are prepared at the same time, the average agreement in potential among the individual electrodes is about 0.02 mv. However, it was found that when electrodes made at different times are compared, they may differ in potential by more than a millivolt, and that an older electrode acts as an anode with respect to a newer one. This aging effect was noted years ago by MacInnes and Parker,[10] who made the following interesting observation: "There was a slight aging effect noticed, the older electrodes

[10] D. A. MacInnes and K. Parker, J. Am. Chem. Soc. 37, 1445 (1915).

being electropositive to the newer ones. As this effect was always in the same direction and of the same magnitude within 0.05 mv no error arose from this source, since similar electrodes were always opposed to each other." Carmody,[11] on the other hand, was unable to confirm an effect of time on the potentials of the electrodes and attributed such changes to the action of light.

Figure 3 shows the data obtained on the aging effect in the case of the electrolytic type of silver-silver chloride electrodes compared in 0.05 *N* air-saturated solution of potassium chloride without stirring. The designations KCl, NaCl, and HCl on the curves signify that the electrodes were chloridized in solutions of potassium chloride,

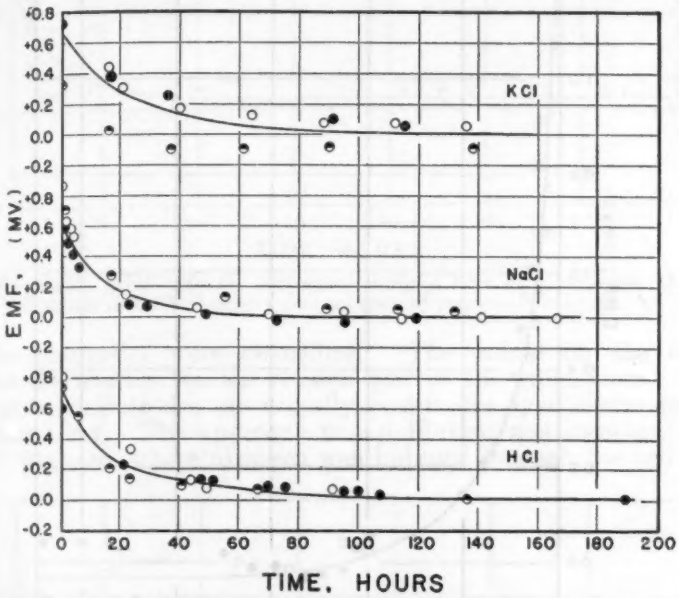

FIGURE 3.—*Aging effect with the electrolytic type of silver-silver chloride electrodes in 0.05 N air-saturated solution of potassium chloride.*

sodium chloride, and hydrochloric acid, respectively. The solution in which they were compared, however, was of potassium chloride. Each point represents the difference between the average potential of four electrodes which had been aged for at least 1 week before use and the average potential of four newer electrodes, plotted against the time in hours. Three independent sets of four newer electrodes, represented by the three different symbols, were used to determine each curve. The zero axis of time represents the time that the newer electrodes were placed in the cell, which was in general about 2 hours after they were chloridized. More than half of the total number of electrodes were measured in a cell blackened to exclude light, the data for which showed that the effect is not due to the action of light. This conclusion is substantiated also by the data given in table 2, which show that electrodes prepared and tested in the absence of light agree closely with others prepared at the same

[11] W. R. Carmody, J. Am. Chem. Soc. 51, 2901 (1929).

time in the presence of light. Accordingly, the light-protected and light-exposed electrodes change in potential with age practically to the same extent. The slopes of the curves are similar, and in every instance freshly prepared electrodes are positive, i. e., they act as cathodes with respect to aged electrodes, the difference approaching zero with time. Although the greater portion of the initial potential difference disappears during the first day, a significant difference still

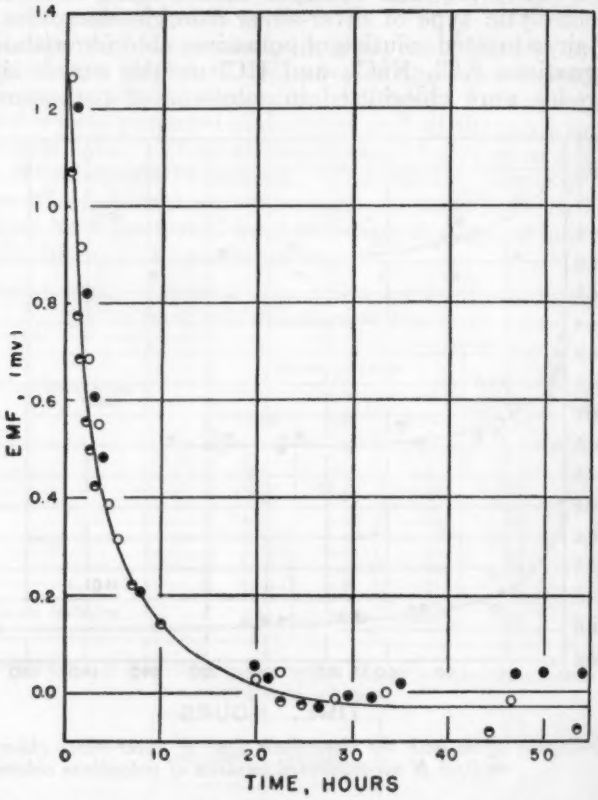

FIGURE 4.—*Aging effect with the electrolytic type of silver-silver chloride electrodes in 0.05 N oxygen-free solution of potassium chloride.*

exists for several days between the newer electrodes and those that have come to equilibrium.

To ascertain whether or not the aging effect is due to the influence of oxygen, cells of the type shown in figure 2 were used. For the electrolytic type, eight electrodes of platinum gauze electroplated with silver and a large silver-silver chloride electrode were placed in the cell containing 0.05 *N* potassium chloride solution. A current of oxygen-free nitrogen was passed through the cell and two of the silver electrodes were chloridized, using the large silver-silver chloride electrode as a cathode. In this way, the silver-silver chloride electrodes were formed without contact with oxygen and without change in the composition of the solution in the cell. After standing several days to allow the freshly formed electrodes to age, a second pair of the silver electrodes was chloridized and then compared in potential

with the first two. On succeeding days the remaining two pairs of electrodes were chloridized and compared with the two aged electrodes. In figure 4, which shows the results obtained with the electrolytic type of electrodes, the zero axis of time was taken almost immediately

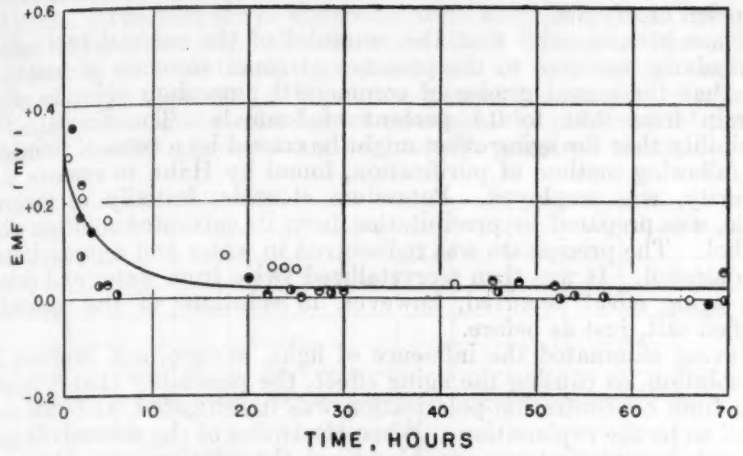

FIGURE 5.—*Aging effect with the thermal-electrolytic type of silver-silver chloride electrodes in 0.05 N oxygen-free solution of potassium chloride.*

after the electrodes were chloridized. The points on the curve represent the average values of each pair at the given time. It is seen that new electrodes are initially positive to aged electrodes by more than 1 mv. The approach to equilibrium was comparatively rapid in this case, where nitrogen was bubbled through the cell con-

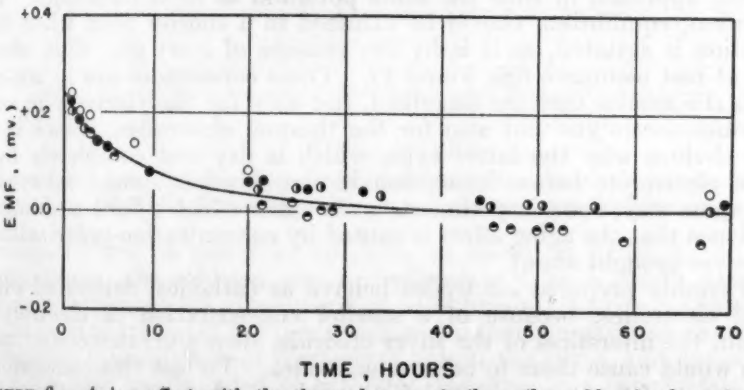

FIGURE 6.—*Aging effect with the thermal type of silver-silver chloride electrodes in 0.05 N oxygen-free solution of potassium chloride.*

tinuously except shortly before and during the times that readings were taken, and an equilibrium potential was reached after approximately 20 hours.

The aging of thermal-electrolytic and thermal electrodes was measured similarly with air excluded by the continuous passage of nitrogen through the solution. The results are shown in figure 5 (thermal-electrolytic) and figure 6 (thermal). While the over-all

change in potential is less than in the case of the electrolytic type, the time required for attainment of equilibrium is about the same, being again more rapid with than without the passage of nitrogen through the solution. It will be seen later that this increased rate is due to the stirring of the solution by the inert gas and not to the exclusion of oxygen.

It has been noted [12] that the potential of the calomel half-cell is particularly sensitive to the presence of small amounts of bromide, and that the purest grades of commercial potassium chloride often contain from 0.01 to 0.1 percent of bromide. To eliminate the possibility that the aging effect might be caused by a trace of bromide, the following method of purification, found by Hahn to remove this impurity, was employed. Potassium chloride, initially of reagent grade, was prepared by precipitation from its saturated solution with alcohol. The precipitate was redissolved in water and reprecipitated with alcohol. It was then recrystallized twice from water and dried. The aging effect occurred, however, in solutions of this specially purified salt, just as before.

Having eliminated the influence of light, oxygen, and bromide in the solution, as causing the aging effect, the possibility that it might arise from concentration-polarization was investigated, and this was found to be the explanation. When electrodes of the electrolytic and thermal-electrolytic types are chloridized, the solution within the pores of the silver chloride coating becomes more dilute than the surrounding solution, and these electrodes, freshly prepared and placed in the measuring solution at the same time should, for this reason, act as cathodes toward electrodes previously aged in the solution, with consequent replenishment of electrolyte within their pores. Also, the freshly prepared electrodes should agree among themselves, except for secondary differences arising from variations in porosity, and should approach in time the same potential as aged electrodes. In addition, equilibrium should be attained in a shorter time when the solution is agitated, as it is by the passage of inert gas, than when left at rest (compare figs. 3 and 4). These conclusions are in accord with the results thus far described, not only for the electrolytic and thermal-electrolytic but also for the thermal electrodes. Since it is not obvious why the latter type, which is dry and completely free from electrolyte before immersion in the solution, should behave in the same way, some experiments were made which afford additional evidence that the aging effect is caused by concentration-polarization, however brought about.

If freshly prepared electrodes behave as cathodes, compared with aged electrodes, because of a smaller concentration of electrolyte within the interstices of the silver chloride, then a greater concentration would cause them to behave as anodes. To test this conclusion, a current of 6 ma was passed for 10 minutes between two thermal-electrolytic electrodes, in a set which had come to equilibrium, to produce mutually opposite concentration-polarization in them. As predicted for such concentration-polarization, the one which had been the anode during passage of the current then behaved as a cathode, and the one which had been the cathode behaved as an anode, toward the aged electrodes. With nitrogen bubbling through the solution, approximately 24 hours' time was required for these two electrodes to

[12] F. L. Hahn, J. Am. Chem. Soc. 57, 2537 (1935).

reattain equilibrium, as shown by agreement again with the aged electrodes.

Four thermally-prepared silver electrodes, two aged thermal-electrolytic silver-silver chloride electrodes and a large silver-silver chloride electrode were placed in a cell containing 0.05 *N* potassium chloride. The four silver electrodes were then chloridized, using the large silver-silver chloride electrode as a cathode. Immediately afterwards, two of these were connected as cathodes to the large electrode and a current of 5 ma was passed to each for 10 minutes. Using the two aged electrodes for reference, the potentials of the two pairs of freshly prepared and oppositely polarized electrodes were

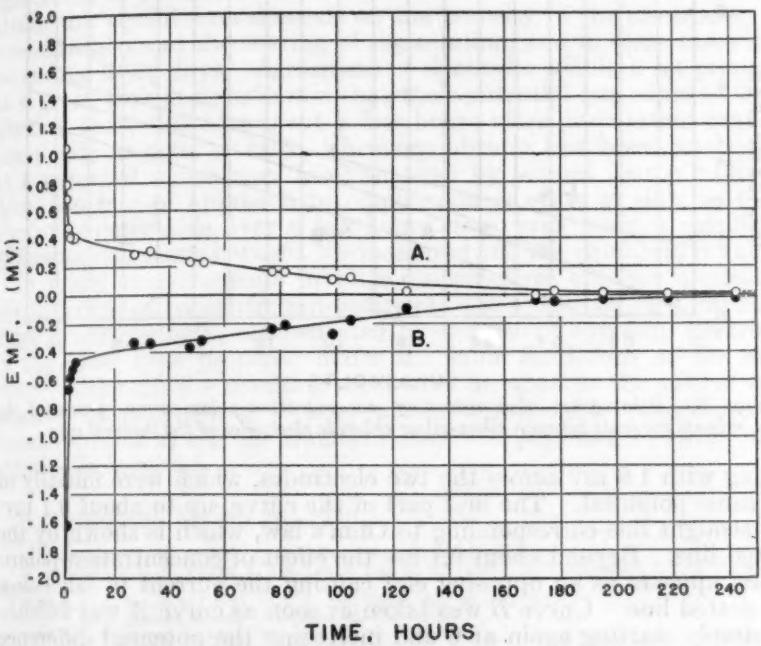

FIGURE 7.—*Aging effect with oppositely polarized silver-silver chloride electrodes of the thermal-electrolytic type in 0.05 N potassium chloride.*

compared over a period of 10 days, as shown in figure 7. In this experiment, the solution was not stirred and, as a result, a longer time was needed for attainment of equilibrium. Curve *A* shows the change in potential of the pair which ended their preparation as anodes, resulting in a dilution of electrolyte within the pores, and curve *B* is for the pair which ended as cathodes, resulting in a concentration of electrolyte within the pores. The two curves together illustrate the effect of concentration-polarization produced in both directions and its direct explanation of the aging effect.

Similar confirmatory data were obtained by soaking one electrode in distilled water and another in 1 *N* potassium chloride, then immersing both in 0.05 *N* potassium chloride and comparing their potentials with that of an electrode aged in the 0.05 *N* solution.

The potential of silver-silver chloride electrodes is sensitive to very small polarizing currents, produced by as little as 0.1 to 0.2 mv between

a pair of them in a cell containing 0.05 N potassium chloride and having an internal resistance of about 250 ohms. This was shown by connecting a pair of closely agreeing thermal electrodes to a polarograph [13] and photographically recording current-voltage curves. The total potential drop across the revolving potentiometer drum was fixed at 1.9 mv by insertion of the proper resistance in the external battery circuit, so that each of the 19 turns of wire on the drum corresponded to only 0.1 mv. If no concentration-polarization occurred, the polarograms would show straight lines, in accordance with Ohm's law, as they did with a wire resistance in place of the cell. In the polarogram of figure 8, curve A is the current-voltage curve beginning with 0 and

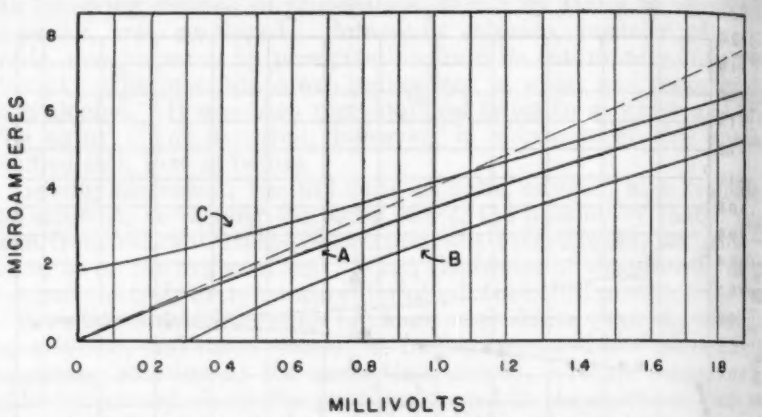

FIGURE 8.—*Polarogram demonstrating concentration-polarization produced by minute currents between silver-silver chloride electrodes of the thermal type.*

ending with 1.9 mv across the two electrodes, which were initially of the same potential. The first part of the curve, up to about 0.1 mv, is a straight line corresponding to Ohm's law, which is shown by the dotted line. Beyond about 0.1 mv the effect of concentration-polarization appears as an opposing emf causing the current to fall below the dotted line. Curve B was taken as soon as curve A was finished by simply starting again at 0 and increasing the potential difference again up to 1.9 mv. This time the electrodes at the start were polarized oppositely and exerted a counter emf to the applied potential difference. The current was therefore negative at the start, being due to the residual concentration-polarization, reached 0 at an applied potential difference of about 0.3 mv, where the emf of the residual concentration-polarization was equal and opposite to the applied potential difference, and then increased at a decreasing rate as additional concentration-polarization was developed. Curve C was taken immediately after curve B was photographed by reversing the electrode connections and going again from 0 to 1.9 mv. Here the applied potential difference and the emf of concentration-polarization are additive, thus producing a current greater than before, which increases at a decreasing rate as the initial concentration-polarization progressively decreases and approaches reversal. The polarogram thus confirms the explanation of the aging effect as a concentration-polarization, and affords a picture of its progress produced artifically, both forwards and backwards, by the passage of very small currents.

[13] J. Heyrovsky in Physikalische Methoden der Analytischen Chemie, II, 260 (Leipzig 1936).

The significant effect of concentration-polarization on the potential of the silver-silver chloride electrode, and the requirement of sufficient aging time to attain concentration equilibrium within the porous silver chloride offer a possible explanation of why certain investigators have noted a drift in potential and reported the thermal-electrolytic type to be more positive than the thermal type,[14] of why others have discarded the electrolytic type as unreliable,[15] and of differences in the values reported for the standard electrode potential of the silver-silver chloride electrode.[16]

It was found in this work that if sufficient time is allowed, the electrolytic, thermal-electrolytic and thermal types finally come to agreement in potential within about 0.02 mv. The time required to attain this equilibrium depends on the porosity of the electrodes, the concentration and the stirring of the solution, and in some cases may be as long as 20 days. Agreement of electrodes within a set prepared at a given time is no criterion that their potential has come to equilibrium, since this agreement a few hours after preparation may be practically as good as later, when equilibrium has been established at a potential which may have changed by several tenths millivolt. Also, the rate of approach to equilibrium is often so slow as to be almost undetectable over a few hours time, even when a significant difference still exists between the measured and the equilibrium values.

In many measurements involving silver-silver chloride electrodes, the influence of concentration-polarization has been at least partially, even if unknowingly, compensated by the use of opposing electrodes of the same type prepared under the same conditions at the same time. Although the resulting error may be small in the case of such relative measurements, it may attain considerable significance in measurements where the standard electrode potential of silver-silver chloride is involved.

WASHINGTON, March 29, 1938.

[14] C. K. Rule and V. K. La Mer, J. Am. Chem. Soc. **58**, 2339 (1936).
[15] M. Randall and L. E. Young, J. Am. Chem. Soc. **50**, 989 (1928). A. S. Afanasiev, J. Am. Chem. Soc. **52**, 3477 (1930).
[16] 0.2238 v. A. A. Noyes and J. H. Ellis, J. Am. Chem. Soc. **39**, 2532 (1917).
0.2234 v. G. A. Linhart, J. Am. Chem. Soc. **41**, 1175 (1919).
0.2226 v. G. Scatchard, J. Am. Chem. Soc. **47**, 641 (1925).
0.2228 v. G. Nonhebel, Phil. Mag. [7] **2**, 1085 (1926).
0.2221 v. M. Randall and L. E. Young, J. Am. Chem. Soc. **50**, 989 (1928).
0.2224 v. E. J. Roberts, J. Am. Chem. Soc. **52**, 3877 (1930).
0.2223 v. W. R. Carmody, J. Am. Chem. Soc. **54**, 188 (1932).
0.2224 v. H. S. Harned and R. W. Ehlers, J. Am. Chem. Soc. **54**, 1350 (1932).
0.2221 v. Int. Crit. Tables **6**, 332 (1929).

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INFLUENCE OF COPPER AND IRON SALTS ON THE BEHAVIOR OF LEATHER IN THE OXYGEN BOMB

By Joseph R. Kanagy

ABSTRACT

Samples of chestnut and quebracho leathers containing from 0.01 to 0.78 percent of copper or iron, were aged in an atmosphere of oxygen at 100 lb/in.^{2} for 7 days at 100° C. The amounts of the nitrogenous materials extractable after this treatment were used as a measure of deterioration. All leathers containing added copper showed more deterioration than the corresponding untreated leathers. In the case of iron, no appreciable increase in the rate of deterioration occurred for values above pH 3.5, and below this value the deterioration appears to be a function of pH rather than of iron content. For equal amounts of metal, that added as the sulfate is more active in accelerating the deterioration of the leathers than that added in the form of the acetate or the lactate.

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I. INTRODUCTION

The deterioration of leather is accelerated by the presence of either copper or iron under certain conditions. Most vegetable-tanned leathers become contaminated with copper and iron during the tanning process. The source of these impurities is the tanning materials which come in contact with these metals, in the grinders and evaporators in which they are prepared. The acidic character of finished leathers causes a further contamination if contact is made in service with surfaces containing these metals. Leathers used for belting and hydraulic packings are most likely to become contaminated by these metals.

The influence of copper and iron on the oxidation of leather and leather-making materials has been studied by a number of investigators. E. W. Merry [1] [1] showed that the addition of copper as copper acetate greatly increased the rate of absorption of oxygen by a solution of American chestnut extract, and that the addition of iron as ferric alum also had an accelerating effect on the absorption of oxygen but

[1] Numbers in brackets indicate references at the end of the paper.

not so great as in the case of copper. R. Faraday Innes [2] studied the effect of iron and copper on leather by accelerated aging with hydrogen peroxide. After experimenting with ferrous sulfate and a copper salt, he concluded that oxidation of either pyrogallol- or catechol-tanned leather is accelerated greatly by iron and to a lesser extent by copper. M. Bergmann [3] and coworkers showed that vegetable-tanned leather was equally damaged by either ferrous sulfate or sulfuric acid solutions having pH values approximately 3.5, which indicated that in this case the effect was not oxidation by the iron but hydrolysis by the acid. J. Jablonski [4] commenting on Bergmann's work believed that deterioration was not observed because air was not freely accessible to the samples. The lack of agreement in the conclusions of these investigators seems to be caused by differences in the conditions under which their experiments were made. This has made desirable a further study of the action of copper and iron salts on leather so that data obtained in the treatment of leathers in the oxygen bomb may be more accurately related to their behavior during normal aging. This investigation consists in a study of the effects produced when leather is impregnated with varying amounts of different salts of these metals and exposed to oxygen in a bomb.

II. MATERIALS AND METHODS

Quebracho- and chestnut-tanned leathers prepared in the experimental tannery at the National Bureau of Standards were used in this investigation. Samples of these leathers were impregnated with varying amounts of copper and iron by soaking in solutions of copper sulfate, copper acetate, ferrous sulfate and ferrous lactate of different concentrations. Ferrous salts were used because they are less readily hydrolyzed at low pH values than the corresponding ferric salts, and for this reason penetrate the leather more readily. The total amounts of these metals in the leathers (see table 1), based on the oven-dry weights of the samples, ranged from 0.01 to 0.78 percent. Although neither copper nor iron is actually present in the leather in metallic form, for convenience, reference is usually made to the quantity in terms of the metal.

The amounts of copper in the leathers were determined [6] as follows: The ash from a 10-g sample was leached with a mixture of sulfuric and nitric acids. After diluting, filtering, and acidifying further with nitric acid the solution was subjected to electrolysis. This treatment deposited most of the copper, which was weighed. The last traces of copper were determined by passing hydrogen sulfide into the electrolyzed solution, filtering and igniting the precipitate and weighing as copper oxide.

In determining the iron [7], the ash was treated in the same way as in the determination of copper. The nitric acid was then removed by heating the solution until white fumes of sulfuric acid were evolved. The solution was diluted and acidified further with concentrated sulfuric acid. The iron was reduced with metallic zinc and then determined by titrating with 0.1 *N* potassium permanganate solution.

In making the tests in the oxygen bomb, pieces of the leathers, approximately 1½ by 3 in., were dried in an oven at 100° C for 24 hours. At the end of this time, they were placed in the bomb in an atmosphere of oxygen at 100 lb/in.^{2} and 100° C, and aged under these conditions for 7 days. The extent of the deterioration was deter-

mined by the percentage of the total amount of the nitrogenous materials extracted from the aged samples by water and 0.1 *N* sodium carbonate solution. The method used in extracting this nitrogenous material and a description of the oxygen bomb used are given in a previous report [5].

III. RESULTS AND DISCUSSION

1. pH CHANGES

In a previous investigation [8] at the National Bureau of Standards on the effects of sulfuric acid on leather, it was found that those leathers, containing sulfuric acid, whose water extracts had pH values below 3, deteriorated most rapidly under normal aging conditions. A study of the behavior of leather in the oxygen bomb [5] also indicated that deterioration occurred most rapidly below pH 3. For these reasons, it is important to consider the pH factor in a study of the effect of copper and iron salts on the deterioration of leather, in order to distinguish between deterioration caused by the hydrolytic action of acids and that caused by the presence of the metals.

When a salt formed by a strong acid and a weak base, such as copper or ferrous sulfate, is dissolved in water, the solution shows an acid reaction. The degree of acidity under these conditions obviously depends in part upon the strength of the acid from which the salt is formed. Solutions of copper acetate and ferrous lactate therefore have higher pH values than those of the sulfates, and when added to leather may be expected to cause a smaller increase in acidity.

The pH values of the various concentrations of salt solutions in which the leathers were soaked, as well as those of the treated leathers before and after exposure in the oxygen bomb, are given in table 1. The intial pH values of the treated leathers are in most cases lower than either that of the solution or that of the original leather, which indicates that a chemical change has taken place between the leather and the salt. This change is probably brought about by the salt reacting with the tannic acid to form an insoluble tannate as shown for ferrous sulfate by the equation, where RCOOH represents the tannic acid.

$$FeSO_4 + 2\ RCOOH \rightleftarrows Fe(RCOO)_2 + H_2SO_4$$

The formation of the insoluble tannate causes this reaction to proceed to the right and form sulfuric acid. The same reaction takes place with the acetates and the lactates, but since these salts form weak acids the pH values are not lowered to the point where deterioration is caused by acidity. This indicates that the influence of acidity has, to a large extent, been eliminated for those leathers treated with copper acetate and ferrous lactate, since none of these samples had pH values below 3.

During exposure in the bomb, the acidity of the leather tends to increase, as shown by a decrease in its pH value. This indicates that weak organic acids are formed by oxidation of the tannins. The magnitude of the pH change depends upon the initial pH and the salt used in impregnating the leather. Leathers with initial pH values above 4 show rather large changes during exposure. At pH values below 4, leathers treated with the sulfates show the largest changes (see table 1). The pH values of the leathers treated with the higher

amounts of the sulfates dropped below 3 during exposure in the bomb. In all cases the pH values of the leathers treated with the lactates and the acetates remained above 3 during exposure.

TABLE 1.—*Data on the effect of copper and iron salts on leather*

Treatment	Treating solution		Quebracho leather				Chestnut leather			
	Concentration	pH	Metal present dry basis	pH changes: Initial	pH changes: After exposure in bomb	Total nitrogen dissolved	Metal present dry basis	pH changes: Initial	pH changes: After exposure in bomb	Total nitrogen dissolved
	Percent		*Percent*			*Percent*	*Percent*			*Percent*
Untreated (copper determined)			0.015	5.20	3.74	4.4	0.04	3.83	3.32	31.7
Copper sulfate	0.19	4.84	.042	4.66	3.56	8.9	.07	3.78	3.44	36.1
Do	.38	4.60	.07	4.54	3.57	11.2	.11	3.61	3.39	37.6
Do	.76		.15	4.27	3.34	24.1	.20	3.49	3.14	46.9
Do	1.52		.31	4.05	3.17	35.8	.33	3.25	3.00	47.6
Do	3.93	3.70	.71	3.71	2.85	64.7	.58	3.09	2.95	68.0
Copper acetate	.16	5.84	.067	5.18	3.62	8.2	.086	3.79	3.27	33.5
Do	.32	5.74	.099	4.79	3.55	11.3	.10	3.84	3.30	40.3
Do	.64	5.60	.19	4.62	3.52	15.8	.22	3.78	3.24	40.7
Do	1.28	5.50	.29	4.45	3.52	17.8	.39	3.76	3.27	41.0
Do	3.20	5.30	.52	4.44	3.54	30.9	.65	3.74	3.28	43.8
Untreated (iron determined)			.009	5.00	3.94	3.1	.020	3.79	3.46	24.0
Do			.012	5.06	3.98	1.8	.023	3.84	3.42	26.4
Ferrous sulfate	.55	3.97	.047	4.40	3.68	3.3	.065	3.62	3.20	40.5
Do	1.11	3.60	.12	3.92	3.47	4.8	.13	3.20	2.96	50.5
Do	2.22	3.59	.21	3.52	3.18	5.7	.19	2.95	2.78	66.3
Do	4.44	3.35	.36	3.34	2.92	11.2	.38	2.70	2.62	88.0
Do	8.88	3.07	.73	3.04	2.63	34.6				
Do	*5.94	3.42	.71	3.24	2.86	13.4				
Do	*7.44	3.30	.76	3.15	2.76	20.9				
Ferrous lactate	.55	5.16	.082	4.44	3.82	2.1	.115	3.64	3.38	25.4
Do	1.11	5.14	.15	4.14	3.71	2.5	.15	3.49	3.32	29.5
Do	2.22	5.10	.21	3.82	3.66	3.3	.26	3.38	3.26	33.6
Do	4.44	4.98	.31	3.60	3.54	4.8	.47	3.22	3.16	46.2
Do	8.88	4.76	.42	3.54	3.50	5.4	.49	3.20	3.20	43.6
Do	14.28	4.42	.65	3.54	3.50	6.6				
Sulfuric acid	0			4.98	3.71	3.6		3.74	3.47	28.6
Do	.17			4.34	3.47	3.6		3.47	3.12	31.5
Do	.35							3.37	2.95	30.3
Do	.68			3.74	3.24	5.6		3.20	2.88	33.1
Do	.85							3.03	2.82	34.6
Do	1.25			3.25	2.92	6.1		2.78	2.64	45.2
Do	1.70			2.78	2.70	12.0		2.68	2.52	47.5
Do	2.50			2.58	2.37	24.6		2.48	2.46	64.3
Do	3.50			2.30	2.28	38.7				

* These two treatments were made with a different sample of ferrous sulfate.

2. EFFECT OF COPPER SALTS ON THE DETERIORATION OF LEATHER

The effect of copper on the deterioration of chestnut- and quebracho-tanned leathers is shown in figures 1 and 2. In figure 1 the extent of the deterioration of the leathers treated with copper sulfate and copper acetate is shown as a function of the initial pH and is compared with that of similar leathers treated only with sulfuric acid. The percentages of copper in the samples are shown beside the plotted points. This comparison indicates that leather is very sensitive to deterioration in the presence of copper. The action of copper appears to be catalytic, since the deterioration takes place in the presence of comparatively small amounts of the metal. The same conclusions

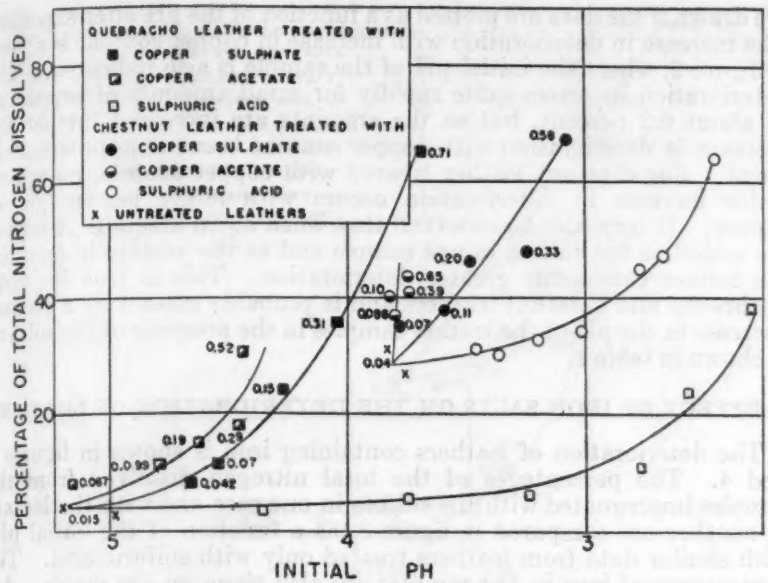

FIGURE 1.—*Increase in the amounts of the total nitrogen dissolved as a function of the initial* pH *values of leathers treated with copper salts, and with sulfuric acid.*

Figures beside the plotted points are the percentages of copper present in the samples.

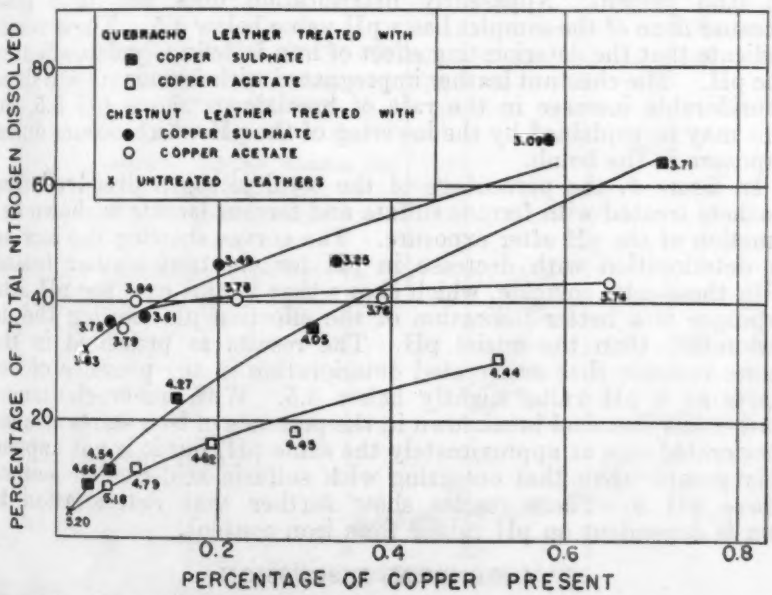

FIGURE 2.—*Increase in the percentages of the total nitrogen dissolved with increase in copper content.*

Figures beside the plotted points are the initial pH values of the samples.

are drawn if the data are plotted as a function of the pH after exposure. The increase in deterioration with increase in copper content is shown in figure 2, where the initial pH of the sample is also indicated. The deterioration increases quite rapidly for small amounts of copper up to about 0.2 percent, but as the amounts are increased further the increase in deterioration with copper content becomes approximately linear. For chestnut leather treated with copper acetate, no appreciable increase in deterioration occurs with larger percentages of copper. It may also be observed that when equal amounts of copper are added as the sulfate in one sample and as the acetate in another, the former causes the greater deterioration. This is true for both quebracho and chestnut leathers and is probably caused by a greater decrease in the pH of the leather samples in the presence of the sulfate, as shown in table 1.

3. EFFECT OF IRON SALTS ON THE DETERIORATION OF LEATHER

The deterioration of leathers containing iron is shown in figures 3 and 4. The percentages of the total nitrogen dissolved from the samples impregnated with the sulfate in one case and with the lactate in another are compared in figure 3, as a function of the initial pH, with similar data from leathers treated only with sulfuric acid. The percentages of iron in the samples are also given on the graph. According to the data, the deterioration of the quebracho leather treated with ferrous sulfate and that of the chestnut leather containing ferrous lactate, is accelerated by iron at pH 3.5 and below. Quebracho leather treated with ferrous lactate shows no appreciable deterioration even though the amounts of iron present vary from 0.08 to 0.65 percent. Apparently deterioration does not take place because none of the samples has a pH value below 3.5. These results indicate that the deteriorating effect of iron is definitely dependent on the pH. The chestnut leather impregnated with ferrous sulfate shows considerable increase in the rate of breakdown above pH 3.5, but this may be explained by the lowering of the pH which occurs during exposure in the bomb.

In figure 4, the percentage of the total nitrogen dissolved from leathers treated with ferrous sulfate and ferrous lactate is shown as a function of the pH after exposure. The curves showing the increase in deterioration with decrease in pH for chestnut leather treated with these salts coincide, which shows that in this case the pH after exposure is a better indication of the effective pH causing the deterioration than the initial pH. The results as presented in this figure indicate that accelerated deterioration in the presence of iron starts at a pH value slightly below 3.5. With quebracho-tanned leather the chemical breakdown in the presence of iron starts at a less accelerated rate at approximately the same pH, but it is not appreciably greater than that occurring with sulfuric acid-treated leathers above pH 3. These results show further that deterioration by iron is dependent on pH rather than iron content.

4. GENERAL DISCUSSION

The mechanism of the action of copper and iron in accelerating the deterioration of leather appears to be catalytic, since deterioration occurs in the presence of comparatively small amounts of the metals. However, the conditions under which the two metals are effective

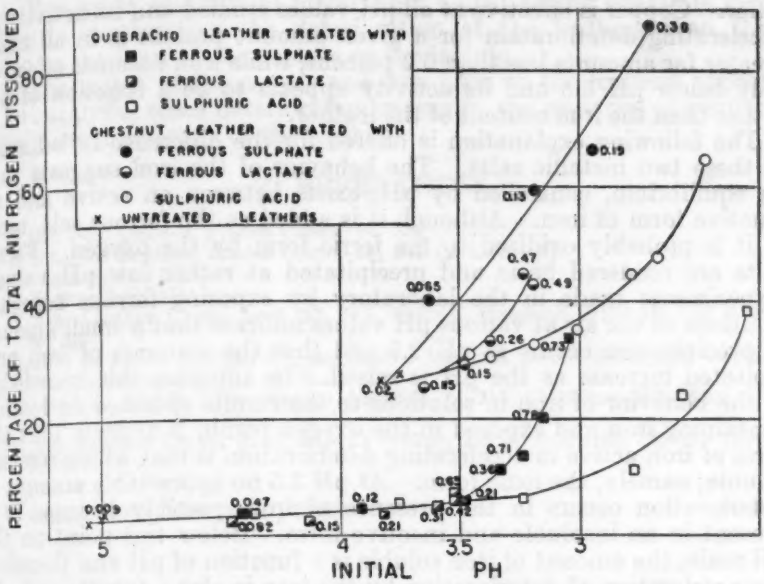

FIGURE 3.—*Increase in the amounts of the total nitrogen dissolved as a function of the initial* pH *values of leathers treated with iron salts and with sulfuric acid.*

Figures beside the plotted points are the percentages of iron present in the samples.

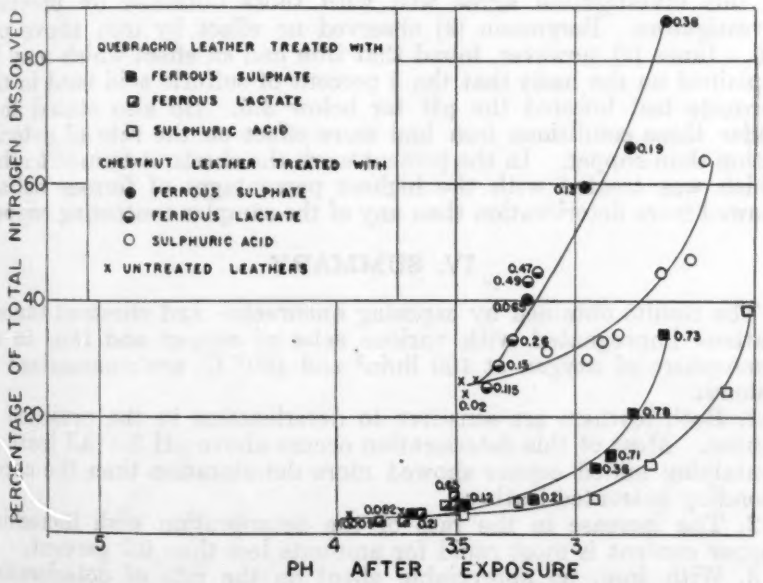

FIGURE 4.—*Increase in the amounts of the total nitrogen dissolved as a function of the* pH *after exposure of leathers treated with iron salts and sulfuric acid.*

Figures beside the plotted points are the percentages of iron present in the samples.

differ. Copper is effective at all pH values studied and its activity in accelerating deterioration for a given amount present is in all cases greater for amounts less than 0.2 percent, while iron becomes effective only below pH 3.5 and its activity appears to be a function of pH rather than the iron content of the leather.

The following explanation is offered for the difference in behavior of these two metallic salts. The behavior of the iron suggests that an equilibrium, controlled by pH, exists between an active and an inactive form of iron. Although it is added as the ferrous salt, most of it is probably oxidized to the ferric form by the oxygen. Ferric salts are rendered basic and precipitated at rather low pH values. Experiments made in the laboratory by exposing ferrous sulphate solutions to the air at various pH values indicate that a small amount of precipitation occurs at pH 2.8 and that the amounts of iron precipitated increase as the pH is raised. In applying this knowledge of the behavior of iron in solutions to the results obtained on leather containing iron and exposed in the oxygen bomb, it appears that the form of iron active in accelerating deterioration is that which remains soluble; namely, the ionic form. At pH 3.5 no appreciable amount of deterioration occurs in the presence of iron, possibly because it is present in an insoluble and inactive form. Below this point on the pH scale, the amount of iron soluble is a function of pH and therefore the acceleration of deterioration by the iron is also a function of pH. For equal amounts of metal added, the sulfates accelerate deterioration of chestnut and quebracho leathers at a greater rate than either the acetates or the lactates, apparently because the sulfates cause a greater increase in acidity.

Where experimental conditions are comparable, the results obtained in this investigation agree well with those obtained by previous investigators. Bergmann [3] observed no effect by iron above pH 3.5. Innes [2], however, found that iron had an effect which may be explained on the basis that the 5 percent of sulfuric acid used in the peroxide test lowered the pH far below 3.5. He also stated that under these conditions iron had more effect on the rate of deterioration than copper. In the present work the chestnut-tanned leather which was treated with the highest percentages of ferrous sulfate showed more deterioration than any of the samples containing copper.

IV. SUMMARY

The results obtained by exposing quebracho- and chestnut-tanned leathers impregnated with various salts of copper and iron to an atmosphere of oxygen at 100 lb/in² and 100° C, are summarized as follows:

1. Both leathers are sensitive to deterioration in the presence of copper. Most of this deterioration occurs above pH 3. All leathers containing added copper showed more deterioration than the corresponding untreated leathers.

2. The increase in the rate of the deterioration with increasing copper content is most rapid for amounts less than 0.2 percent.

3. With iron, no appreciable effect on the rate of deterioration occurs above pH 3.5 and at lower pH values the deterioration appears to be a function of pH rather than iron content.

4. For equal amounts of metal, that added as the sulfate is more active in accelerating the deterioration of the leathers than that added in the form of the acetate or the lactate.

5. The action of the copper and iron salts on the leathers appears to be catalytic, since deterioration occurs in the presence of comparatively small amounts of the metals.

V. REFERENCES

[1] J. Int. Soc. Leather Trades Chem. **16,** 239 (1932).
[2] J. Int. Soc. Leather Trades Chem. **19,** 109 (1935).
[3] Collegium 451 (1934).
[4] Collegium 7 (1935).
[5] J. Am. Leather Chem. Assn. **32,** 314, 1937; J. Research NBS **18,** 713 (1937) RP1004.
[6] Harold A. Fales, Inorganic Quantitative Analysis, p. 389–390 (The Century Co., New York, N. Y., 1925).
[7] Edward G. Mahin, Quantitative Analysis, p. 218, (McGraw-Hill Book Co. New York, N. Y., 1924).
[8] J. Am. Leather Chem. Assn. **28,** 125 (1933); BS J. Research **10,** 559 (1933) RP547.

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